

ON THE OXIDATION OF HYDRAZINE

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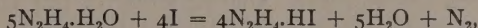
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The author takes great pleasure in expressing his deepest gratitude to Professor A. W. Browne, under whose direction and with whose assistance this work was carried out. To Professor L. M. Dennis, the head of the department of chemistry, and to Professors Bancroft and Chamot the author is also deeply indebted for the many kindnesses shown him during his stay at Cornell University.

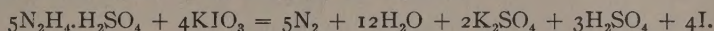
ON THE OXIDATION OF HYDRAZINE. I.

Curtius and Schulz¹ have shown that alcoholic solutions of hydrazine hydrate and iodine react quantitatively in accordance with the equation



and that this reaction may be used as the basis of a method for determining the strength of solutions of hydrazine hydrate.

Rimini² found that the reaction between hydrazine sulphate and potassium iodate could be expressed by the equation



For the determination of hydrazine he recommended the following procedure: A weighed sample of the material to be examined is treated with a measured excess of potassium iodate. After the solution has been heated (in order to expel the liberated iodine) and then cooled, it is acidified with dilute sulphuric acid, and the excess of potassium iodate is determined in the usual way with a standard solution of sodium thiosulphate. Rimini stated that bromates react with hydrazine, when heated, but that chlorates do not react at all.

Riegler³ devised a method for the determination of formaldehyde, which consists in the measurement of the volume of nitrogen liberated from a known amount of hydrazine sulphate (in presence of the formaldehyde) by the action of a solution of iodic acid. From the difference between the volume of nitrogen formed under these conditions, and the volume liberated from the same amount of hydrazine sulphate (in absence of formaldehyde), may be calculated the amount of formaldehyde present. In a subsequent article⁴ Riegler suggested the use of a gasometric method of alkalimetry, based upon the reaction between hydrazine sulphate and sodium iodate. Still later⁵ he recommended for the determination of iodides, a method consisting in the measurement of the nitrogen liberated by the addition of an excess of hydrazine sulphate to the iodate solution obtained by oxidizing the iodide in alkaline solution with potassium permanganate.

Stollé⁶ described an iodometric method for the determination of hydrazine. The titration is carried out in the presence of primary potassium or sodium carbonate. Rupp⁷ maintained that the presence of

¹ J. pr. Chem. [2], 42, 521-49 (1890).

² Gazz. chim. ital., 29, I, 265-69 (1899); Atti. accad. Lincei Roma [5], 15, II, 320; Chem. Zentr., 1906, II, 1662.

³ Z. anal. Chem., 40, 92-4 (1901).

⁴ *Ibid.*, 41, 413-19 (1902).

⁵ *Ibid.*, 46, 315-18 (1907).

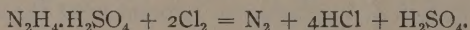
⁶ J pr. Chem. [2], 66, 332-38 (1902).

⁷ *Ibid.* [2], 67, 140-42 (1903).

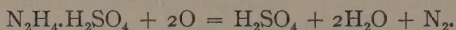
sodium potassium tartrate or sodium acetate leads to more satisfactory results, but that the necessary delay of 15 minutes in awaiting the end of the reaction detracts from the practical value of the iodometric method.

Schlötter¹ found that the reduction of the alkali bromates with hydrazine sulphate proceeds quantitatively, and made use of this fact in his gas volumetric method for the determination of bromates². He also ascertained that iodic acid may be reduced quantitatively to hydriodic acid, by the action of hydrazine sulphate, but that potassium chlorate undergoes quantitative reduction only after prolonged boiling.³

Roberto and Roncali⁴ expressed the reaction between chlorine water and hydrazine sulphate by means of the equation



They recommended the use of hydrazine sulphate in the analysis of chloride of lime and of Javelle solution. In a later article⁵ they have described the action of oxidizing agents upon hydrazine sulphate with the aid of the following general equation:



After expressing the reaction between potassium permanganate and hydrazine sulphate in acid solution by means of an erroneous equation,⁶ they predicted the probable usefulness of hydrazine sulphate in the analysis of oxidizing agents in general, including peroxides and chlorates.

Jannasch and Jahn⁷ found that in alkaline solutions potassium iodate and potassium bromate are easily reduced by hydrazine sulphate, but that potassium chlorate is decomposed only to a limited extent. When potassium chlorate is treated with hydrazine sulphate in the presence of hydrogen peroxide and nitric acid, considerable quantities of hydronitric acid are formed. This result was tacitly attributed by Jannasch and Jahn to the action of nitric acid⁸ upon the hydrazine sulphate, in accordance with the observations of Sabanejeff and Dengin.⁹

¹ Z. anorg. Chem., 37, 164-71 (1903).

² *Ibid.*, 37, 172-76 (1903).

³ *Ibid.*, 38, 184-90 (1904).

⁴ L'Industria chimica, 6, 93-5 (1904); Chem. Zentr., 1904, I, 1294.

⁵ L'Industria chimica, 6, 178-79 (1904); Chem. Zentr., 1904, II, 616.

⁶ Compare Petersen, Z. anorg. Chem., 5, 1-7 (1893); also Medri, Gazz. chim. ital., 36, I, 373 (1906); Chem. Zentr., 1906, II, 459.

⁷ Ber., 38, 1576-89 (1905).

⁸ In the light of certain experiments performed in this laboratory (Browne, This Journal, 27, 551-55 (1905); see also the results shown in Table I of the present article) it is apparent that the formation of hydronitric acid under the conditions prevailing in the experiments of Jannasch and Jahn might also be attributed to the action of either one or both of the other oxidizing agents present: hydrogen peroxide and potassium chlorate.

⁹ Z. anorg. Chem., 20, 21-29 (1899).

The present article contains the description of a series of experiments illustrating the respective action of potassium chlorate, potassium bromate, potassium iodate, chlorine, bromine, and iodine upon hydrazine sulphate in acid solution. These experiments have been performed primarily for the purpose of investigating the possible formation of hydronitric acid as one product of the above reactions, and of determining the yield of the acid under certain specified conditions.

Preparation of Solutions.—The solution of hydrazine sulphate contained 10.000 grams of the salt per liter. The solutions of potassium chlorate, bromate, and iodate contained 9.4226, 12.8418 and 16.4575 grams of the respective salts per liter. All four solutions were therefore almost exactly equimolecular.

General Procedure Followed in the Experiments.—A measured volume of the hydrazine sulphate solution was placed in a one liter round bottom flask provided with a four-hole rubber stopper through which passed (1) the stem of a separatory funnel, (2) a thermometer, (3) a glass tube serving as the air inlet, and reaching to the bottom of the flask, and (4) a glass elbow tube communicating with the condenser. After the desired amount of concentrated sulphuric acid had been added, the solution was heated to about 80° , and a measured amount of the oxidizing agent was added drop by drop through the separatory funnel. Throughout the entire experiment a current of air was in general drawn through the apparatus, in order to carry the hydronitric acid from the flask through the condenser into the absorption apparatus (which contained 5 cc. of a 10 per cent. solution of silver nitrate, 2 cc. of a 10 per cent. solution of sodium acetate and 35 cc. of distilled water), for a description of which reference may be made to the first article of the present series.¹ After the entire quantity of the oxidizing agent had been added, the solution was boiled until all of the hydronitric acid had been distilled from the flask. In the quantitative experiments the amount of hydronitric acid formed was determined as usual by the method of Dennis and Isham.² In certain experiments the yields of ammonia were determined by making the residual solution (after the hydronitric acid had been completely expelled) alkaline with sodium hydroxide and distilling with usual precautions into standard hydrochloric acid. The yields of both hydronitric acid and ammonia have been calculated on the basis of the equation³

¹ Browne and Shetterly, J. Am. Chem. Soc., 29, 1305-12 (1907).

² *Ibid.*, 29, 18 (1907).

³ This equation recalls the work of E. Fischer (Ber., 10, 1336 (1877)), who obtained diazobenzenimide and aniline (analogous to hydronitric acid and ammonia) by the action of iodine upon phenylhydrazine. This analogy in the behavior of the organic and the inorganic derivatives of hydrazine, as well as the interesting question of the possible formation of certain new inorganic compounds of hydrogen and nitrogen as intermediate products of the oxidation of hydrazine, is now under investigation in this laboratory, and will be discussed in detail in a future communication.



Results Obtained in the Experiments.—The results are tabulated under five different heads: (1) action of potassium chlorate upon hydrazine sulphate; (2) action of potassium bromate upon hydrazine sulphate; (3) action of potassium iodate upon hydrazine sulphate; (4) action of chlorine, bromine and iodine, respectively, upon hydrazine sulphate; (5) action of potassium chlorate, bromate and iodate, respectively, upon hydrazine sulphate in presence of silver sulphate.

(1) *Action of Potassium Chlorate upon Hydrazine Sulphate.*—When heated together in presence of free sulphuric acid, aqueous solutions of these substances react with the formation of considerable quantities of hydronitric acid and ammonia. The acid was identified by the series of qualitative tests described in an earlier article.¹ The details of a number of experiments are given in Table I.

TABLE I.

Number of experiment.	N ₂ H ₄ .H ₂ SO ₄ solution. cc.	KClO ₃ solution. cc.	Concentrated H ₂ SO ₄ cc.	AgCl obtained. Gram.	Yield HN ₃ . Per cent.	Portion of distillate containing bulk of HN ₃ .
1	100	28.6	10.0	0.0738	13.39	..
2	100	28.6	10.0	0.0840	15.24	..
3	100	33.3	10.0	0.0814	14.77	..
4	100	33.3	10.0	0.0874	15.86	..
5	100	50.0	0.5	0.0204	3.70	6
6	100	50.0	5.0	0.1207	21.90	5
7	100	50.0	10.0	0.0822	14.91	4 and 5
8	100	50.0	25.0	0.0942	17.09	1 and 2
9	100	50.0	50.0			1
10	100	55.6	0.5	0.0299	5.42	6
11	100	55.6	5.0	0.0426	7.73	5
12	100	55.6	10.0	0.0947	17.18	4 and 5
13	100	55.6	25.0	0.0513	9.30	1 and 2
14	100	55.6	50.0			1
15	100	66.7	10.0	0.1091	19.79	..
16	100	66.7	10.0	0.1237	22.44	..

From these experiments it is apparent that the yield of hydronitric acid does not vary in any regular way with the concentration of the oxidizing agent or of the sulphuric acid. In fact, the magnitude of the yield seems to depend fully as much upon the method adopted in bringing the two substances together, in heating the mixture, and in distilling off the hydronitric acid, as upon any other factor. The liberation of chlorine during the experiment militates against the production of a large yield of the acid. That the presence of a considerable amount of sulphuric acid is necessary seems to be shown by the low yields obtained in Experiments 5 and 10. A separate series of experiments (each performed in duplicate), the results of which are given in column 7 of Table I, has

¹ Browne, J. Am. Chem. Soc., 27, 551-55 (1905).

shown, moreover, that the formation of hydronitric acid takes place most readily within a certain range of concentration of sulphuric acid. In each of these experiments the distillate was divided into six 25 cc. fractions. To each fraction was added 1 cc. of a 9 per cent. ferric chloride solution. From the depth of color shown by the various fractions the relative amounts of hydronitric acid present were then roughly estimated. In every case the bulk of the acid was found in one or at most two of the fractions; moreover, as the concentration of sulphuric acid was increased, the formation of the hydronitric acid took place earlier in the experiment. Thus in Experiments 5 and 10, in which but 0.5 cc. of sulphuric acid was present, the hydronitric acid came over in the sixth fraction, while in Experiments 9 and 14, in which 50 cc. of sulphuric acid were present, the hydronitric acid appeared in the first fraction. These facts cannot be explained on the ground that hydronitric acid might be expected to distil over more rapidly from solutions strongly acidified than from solutions but slightly acidified with sulphuric acid. Curtius and Rissom¹ have shown that when an aqueous solution of hydronitric acid is distilled, almost the entire amount of the acid passes over with the first fourth of the liquid. It is consequently legitimate to infer from the presence of the greater part of the hydronitric acid in the sixth fraction obtained in Experiments 5 and 10, for example, that the formation of the acid does not readily take place until toward the close of the experiment, when the concentration of the sulphuric acid has become sufficiently high.

For the purpose of determining the yield of ammonia formed under conditions substantially similar to those under which the largest yield of hydronitric acid had been obtained, four additional experiments were performed. Care was of course taken to use sufficient potassium chlorate to insure the complete oxidation of the hydrazine, since any hydrazine remaining unoxidized would have been at least in part distilled over with the ammonia when the residual solution was heated after having been made alkaline. In each of the experiments, 100 cc. of the hydrazine sulphate solution and 10 cc. of concentrated sulphuric acid were employed. In the first two, 66.7 cc. of the potassium chlorate solution were used in each case; in the last two, 77.8 cc. The yield of ammonia in the four experiments amounted respectively to 48.76, 40.99, 31.64 and 30.06 per cent.

(2) *Action of Potassium Bromate upon Hydrazine Sulphate.*—Aqueous solutions of these substances react when heated together in presence of free sulphuric acid, forming appreciable quantities of hydronitric acid and ammonia. The results obtained in a series of experiments (parallel in the main with the experiments in which potassium chlorate was used) are shown in Table II.

¹ J. pr. Chem. [2], 58, 261-309 (1898).

The best yields of hydronitric acid were obtained when 5 cc. of sulphuric acid were taken. The decrease in yield observed as the concentration of sulphuric acid was increased beyond this limit is at least partially attributable to the greater difficulty of preventing, in strongly acid solution, the liberation of free bromine during the course of the reaction.

TABLE II.

Number of experiment.	$\text{N}_2\text{H}_4 \text{ H}_2\text{SO}_4$ solution. cc.	KBrO_3 solution. cc.	Concentrated H_2SO_4 . cc.	AgCl obtained. Gram.	Yield HN_3 Per cent.
1	100	28.6	5.0	0.0298	5.41
2	100	28.6	10.0		
3	100	33.3	5.0	0.0368	6.68
4	100	33.3	10.0	0.0217	3.94
5	100	50.0	0.0	0.0058	1.05
6	100	50.0	0.5	0.0104	1.88
7	100	50.0	5.0	0.0341	6.18
8	100	50.0	10.0	0.0252	4.57
9	100	55.6	0.5	0.0179	3.25
10	100	55.6	5.0	0.0346	6.28
11	100	55.6	10.0	0.0095	1.72
12	100	55.6	25.0	0.0017	0.31

The yield of ammonia was determined in four additional experiments, in each of which 100 cc. of hydrazine sulphate solution were taken. The other details were respectively as follows: potassium bromate solution, 66.7, 66.7, 77.8, 77.8 cc.; concentrated sulphuric acid, 5, 10, 5, 10 cc.; yield of ammonia, 9.77, 3.91, 1.21, 1.21 per cent.

(3) *Action of Potassium Iodate upon Hydrazine Sulphate.*—Preliminary experiments seemed to indicate that no hydronitric acid was formed by the interaction of these substances. In the four experiments subsequently performed, distilled water was consequently substituted for the usual absorbing solution (containing silver nitrate and sodium acetate), in order to facilitate the detection of minute amounts of hydronitric acid. In each of the experiments 100 cc. of hydrazine sulphate solution were employed. The amounts of the other substances were respectively as follows: potassium iodate solution, 28.5, 33.3, 50, 50 cc.; concentrated sulphuric acid, 5, 5, 5, 10 cc. Some difficulty was experienced in keeping the iodine that was liberated during the reaction from passing over into the distillate, especially in the fourth experiment, in which 10 cc. of sulphuric acid were employed. In certain cases it was found necessary to shake a portion of the distillate (to be tested for hydronitric acid) with metallic mercury before adding the ferric chloride solution, in order to remove the small quantities of free iodine that were unavoidably distilled over. In no case was the slightest indication of the presence of hydronitric acid observed.

In the fifth experiment 200 cc. of the hydrazine sulphate solution, to

which had been added 20 cc. of sulphuric acid, were treated with 133.3 cc. of the potassium iodate solution. The solution was heated until the evolution of gas had ceased, and was then made alkaline with sodium hydroxide. No indication of the presence of ammonia was observed when a moistened piece of red litmus paper was suspended above the liquid in the flask. The subsequent addition of 2 mg. of solid ammonium chloride (corresponding to 0.5 per cent. yield of ammonia) to the same solution caused the litmus paper to turn distinctly blue.

(4) *Action of Chlorine, Bromine, and Iodine, Respectively, upon Hydrazine Sulphate.*—In the foregoing experiments it was observed (as might have been expected) that the tendency for the free halogen to appear during the course of the reaction varied directly with the atomic weight of the halogen. In the experiments with potassium chlorate, for example, it was comparatively easy to keep the free chlorine from passing over into the absorption apparatus, while in the experiments with potassium iodate it was found necessary to employ some caution in the addition of the oxidizing agent, and in the regulation of the temperature at which the reaction was permitted to take place, in order to prevent the carrying over of considerable quantities of free iodine. In almost every case it was found possible, however, by the exercise of proper precautions, to effect the reduction of the free halogen by the hydrazine sulphate still remaining in the solution. From these facts it is obvious that the hydrazine sulphate is in each case virtually subject to the action of two different oxidizing agents during the course of the experiment, either one or both of which might be responsible for the production of the hydronitric acid.

In order to investigate qualitatively the behavior of the free halogens toward hydrazine sulphate, with reference to the formation of hydronitric acid, a series of experiments was performed in which hydrazine sulphate was treated in both acid and alkaline solution with chlorine, bromine

TABLE III.

Number of experiment.	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ solution, cc.	Oxidizing solution, cc.	Conc. H_2SO_4 , cc.	NaOH, Grams.	Result of tests for HN_3 .
1	50	100 (chlorine)	5	.	Small amount of HN_3 .
2	50	100 "	5	.	" " " "
3	50	100 "	.	5	" " " "
4	50	100 "	.	5	" " " "
5	50	100 (bromine)	5	.	No HN_3 .
6	50	100 "	5	.	" "
7	50	100 "	.	5	Trace of HN_3 .
8	50	100 "	.	6	" "
9	50	100 (iodine)	5	.	No HN_3 .
10	50	100 "	5	.	" "
11	50	100 "	.	5	" "
12	50	100 "	.	5	" "

and iodine solutions, respectively. The chlorine solution was prepared (immediately before the experiments were performed) by saturating distilled water at room temperature with chlorine gas. The bromine solution contained about 6.9 grams of bromine per liter. The iodine solution contained about 11.0 grams of iodine, and 22 grams of potassium iodide per liter. The details of the experiments are given in Table III.

For the experiments in which sulphuric acid was used the general procedure was briefly as follows: the oxidizing solution was first added slowly to the acidified hydrazine sulphate solution, with frequent shaking in order to hasten the reaction. When the reduction of the halogen was complete (in the experiments with iodine it was found necessary to heat the solution at intervals), the solution was distilled, and the first fractions were carefully tested for hydronitric acid. For the experiments in which sodium hydroxide was used, the general procedure was as follows: The oxidizing solution was first brought into contact with the sodium hydroxide (in the form of a 20 per cent. solution). The hydrazine sulphate was then added, and the solution was shaken until the evolution of gas had nearly ceased. After having been heated for a short time, the solution was slightly acidified with sulphuric acid and was distilled. Careful tests for hydronitric acid were made, as before, upon the first fractions of the distillate. In no case were indications given of the formation of any very considerable quantity of hydronitric acid. When chlorine was used it was found that a small amount of hydronitric acid was formed in both acid and alkaline solution. With bromine, traces of the acid were formed in alkaline solution, but none in acid solution. With iodine there was no formation of hydronitric acid in either acid or alkaline solution. From these results the conclusion may be drawn that the tendency of the free halogens to form hydronitric acid as one of the oxidation products of hydrazine sulphate is but slight in any case, and that this tendency varies inversely with the atomic weight of the halogen.

It seems reasonable also to infer that the liberation of the halogens in the chlorate, bromate and iodate experiments must be unfavorable to the production of large yields of hydronitric acid, even though precautions are taken to keep the free halogen in any case from passing over into the absorption apparatus. Since the liberation of a given amount of iodine would presumably militate more strongly against the production of hydronitric acid than would the liberation of a corresponding amount of bromine or of chlorine, and since the liberation of iodine takes place more extensively than that of the other halogens, it is by no means surprising that hydronitric acid was not formed in the experiments with potassium iodate. It has moreover been shown by experiment that even potassium chlorate, under conditions otherwise very favorable to the formation of hydronitric acid, does not produce appreciable yields of the

acid in presence of potassium iodide. Two experiments were performed in which the procedure adopted in Experiments 6 and 16, Table I, was carefully duplicated. In these cases, however, 0.64 gram and 0.85 gram of potassium iodide were dissolved in the acidified hydrazine sulphate solution before the (gradual) addition of the potassium chlorate solution. In both cases the tests for hydronitric acid gave negative results.

(5) *Action of Potassium Chlorate, Bromate and Iodate, Respectively, upon Hydrazine Sulphate in Presence of Silver Sulphate.*—A natural supposition to be made on the basis of the facts discussed in the preceding paragraphs is that if the liberation of halogen in the chlorate, bromate, and iodate experiments could be entirely prevented, the yield of hydronitric acid might be appreciably increased. In the experiments recorded in Table IV this condition has been realized by the addition in each case, of 1 gram of silver sulphate, in solid form, to the acidified solution of hydrazine sulphate, prior to the introduction of the oxidizing solution. The procedure was in all other particulars the same as in the earlier experiments with these oxidizing agents.

TABLE IV.

Number of experiment.	N ₂ H ₄ . H ₂ SO ₄ solution. cc.	Oxidizing solution. cc.	Concentrated H ₂ SO ₄ . cc.	AgCl obtained. Gram.	Yield HN ₃ Per cent.	Yield NH ₃ Per cent.
1	100	(KClO ₃) 78.0	10	0.0734	13.32	15.64
2	100	" 78.0	10	0.0707	12.83	16.96
3	100	(KBrO ₃) 66.7	10	0.0374	6.79	25.25
4	100	" 66.7	10	0.0642	11.65	27.42
5	100	(KIO ₃) 66.7	10	0.0520	9.43	12.68
6	100	" 66.7	10	0.0615	11.16	16.16

These experiments show clearly that while in the case of the chlorate solution the presence of silver sulphate does not increase the yield of hydronitric acid, with the bromate solution a slight increase, and with the iodate solution a very marked increase is to be noted. In other words, the influence of the silver sulphate in augmenting the tendency of the chlorate, bromate, and iodate solutions to form hydronitric acid from hydrazine sulphate in acid solution, varies directly with the atomic weight of the halogen.

Summary.

When potassium chlorate or bromate is brought into contact with hydrazine sulphate in the presence of sulphuric acid, the hydrazine is not completely oxidized to nitrogen and water. A secondary reaction takes place which may be expressed by the equation



With potassium chlorate the highest yields obtained were 22.44 per cent. HN₃, 48.76 per cent. NH₃; with potassium bromate, 6.68 per cent. HN₃, 9.77 per cent. NH₃. With potassium iodate under similar con-

ditions no formation of HN_3 or of NH_3 was observed. The amount of hydronitric acid formed, consequently, decreases with increase of the atomic weight of the halogen.

By the action of the free halogens upon hydrazine sulphate but little hydronitric acid was obtained in any case. When chlorine was used, a small amount of the acid was formed in both acid and alkaline solution. With bromine, traces were formed in alkaline solution, but none in acid solution. With iodine there was no formation of hydronitric acid in either acid or alkaline solution. The slight tendency of the free halogens to produce hydronitric acid from hydrazine sulphate, consequently decreases with increase of the atomic weight of the halogen.

The maximum yields of hydronitric acid and ammonia obtained in a series of experiments with potassium chlorate, bromate, and iodate, in the presence of sulphuric acid and silver sulphate, were as follows: with potassium chlorate, 13.32 per cent. HN_3 , 16.96 per cent. NH_3 ; with potassium bromate, 11.65 per cent. HN_3 , 27.42 per cent. NH_3 ; with potassium iodate, 11.16 per cent. HN_3 , 16.16 per cent. NH_3 . The influence of the silver sulphate in augmenting the yield of hydronitric acid consequently varies directly with the atomic weight of the halogen.

The behavior of a number of other oxidizing agents toward hydrazine sulphate is now under investigation in this laboratory.

CORNELL UNIVERSITY,
October, 1907.

ON THE OXIDATION OF HYDRAZINE. II.

The present article contains the description of a series of experiments upon the behavior of hydrazine sulphate in aqueous solution toward the following oxidizing agents: potassium persulphate, potassium permanganate, hydrogen peroxide, potassium perchlorate, sodium periodate, lead dioxide, red lead and manganese dioxide. The experiments have been performed primarily for the purpose of investigating the possible formation of hydronitric acid and ammonia as products of the reaction between these oxidizing agents and hydrazine sulphate, and for the purpose of determining the yield of these products under certain specified conditions. Inasmuch as hydrazine has been employed by Pannain¹ and by Rimini² in the determination of persulphates, while potassium permanganate has been used (1) in acid solution by Petersen,³ and by Roberto and Roncali,⁴ and (2) in alkaline solution by Sabanejeff⁵ for the determination of hydrazine, and since Roberto and Roncali⁶ have suggested the use of hydrazine sulphate in the analysis of oxidizing agents in general, including peroxides and chlorates,⁷ it has also been considered advisable to ascertain whether hydronitric acid is formed under conditions so far as possible corresponding to those recommended by these authors. The procedure followed throughout this work is in general similar to that described in the earlier articles of this series,⁸ unless otherwise specified. The identity of the hydronitric acid was in each case established by means of the usual tests,⁹ and the yield was determined either by the method of Dennis and Isham,¹⁰ in case a fairly large amount of the acid was formed, or by means of an approximate colorimetric method¹¹ in case the amount formed was rather small.

Reaction between Hydrazine Sulphate and Potassium Persulphate in the Presence of Sulphuric Acid.—Aqueous solutions of hydrazine sulphate and potassium persulphate, when heated together in the presence of free sulphuric acid, react with formation of considerable quantities of hydronitric acid and ammonia. This fact was discovered during the

¹ *Gazz. chim. ital.*, 34 (I), 500 (1904).

² *Atti accad. Lincei* (5), 15, II, 320-5 (1906); *Chem. Zentralbl.*, 1906, II, 1662.

³ *Z. anorg. Chem.*, 5, 1 (1893).

⁴ *L. Industria chimica*, 6, 178 (1904); *Chem. Zentralbl.*, 1904, II, 616.

⁵ *Z. anorg. Chem.*, 20, 21-9 (1899).

⁶ *Loc. cit.*

⁷ With reference to the behavior of hydrazine sulphate toward potassium chlorate, see *J. Am. Chem. Soc.*, 30, 53-63 (1908).

⁸ *Ibid.*, 29, 1305-12 (1907); 30, 53-63 (1908).

⁹ *Ibid.*, 27, 551-5 (1905).

¹⁰ *Ibid.*, 29, 18 (1907).

¹¹ The procedure adopted in effecting the approximate color metric determination of small quantities of hydronitric acid in pure aqueous solution, is briefly as follows: to equal amounts of an aqueous solution of ferric chloride, contained in two cylindrical

performance of two preliminary experiments, and has been confirmed by a series of twelve experiments, the results of which are recorded in Table I.

The purity of the potassium persulphate employed throughout these experiments is attested by the results obtained in three determinations of the oxidizing power of the substance. These determinations were effected by a method essentially the same as that described by Treadwell and Hall.¹ The results obtained were as follows: Percentage of available oxygen in potassium persulphate, found, 5.89, 5.89, 5.89; theory, 5.92. With the aid of suitable blank experiments it was demonstrated that none of the materials employed contained any appreciable trace of ammonia, and that no hydronitric acid was produced by the interaction of sulphuric acid and hydrazine sulphate.

TABLE I.

No. of experiment.	N ₂ H ₄ .H ₂ SO ₄ (10 grams per liter). cc.	K ₂ S ₂ O ₈ . Grams.	Conc. H ₂ SO ₄ . cc.	AgCl obtained. Gram.	Yield HN ₃ . Per cent.	NH ₃ obtained. Gram.	Yield NH ₃ . Per cent.
1	100	4.183	1	0.0178	3.23	0.0974	(148.9)
2	100	4.183	2.5	0.0447	8.11	0.0689	(105.2)
3	100	4.183	4	0.0639	11.6	0.0549	83.9
4	100	4.183	5	0.1159	21.0	0.0388	59.3
5	100	4.183	5	0.1526	27.7	0.0348	53.1
6	100	4.124	5	0.0904	16.4	0.0591	90.3
7	100	4.124	5	0.1152	20.9	0.0513	78.3
8	100	4.183	10	0.1565	28.4	0.0365	55.7
9	100	4.183	25	0.1990	36.1	0.0338	51.7
10	100	4.183	25	0.2037	37.0	0.0301	46.0
11	100	4.183	50	0.2154	39.1	0.0303	46.4
12	100	4.183	50	0.2223	40.3	0.0296	45.2

In all of the above experiments, with the exception of Experiments 6 and 7, the procedure was essentially as follows: The hydrazine sulphate solution and the solid potassium persulphate were placed together in a 1000 cc. distilling flask connected with a condenser and with the usual absorption apparatus. The concentrated sulphuric acid was then

vessels of the same size and shape, are added respectively a measured volume of the solution in which the percentage of hydronitric acid is to be determined, and a measured volume of a standard solution of hydronitric acid. The standard solution is added drop by drop, until the color intensity of the two solutions, after they have been brought to equal volume by dilution of one or the other with water, is exactly the same. The percentage of hydronitric acid in the solution of unknown strength may be calculated from the proportion

$$C_1 : C_2 = V_2 : V_1$$

in which C_1 and C_2 represent the respective percentages of hydronitric acid in the standard solution and in the solution of unknown strength, and in which V_1 and V_2 represent the volumes of the two solutions added.

¹ *Analytical Chemistry*, Vol. II., 495 (1907).

added drop by drop, and the solution was heated until the complete removal of the hydronitric acid had been effected. In order to accomplish this end it was usually found necessary to add 25 cc. of water, after the greater part of the water in the flask had been distilled over, and then to continue the distillation until white fumes just began to appear in the flask. It was found that in Experiments 9, 10, 11 and 12, the hydronitric acid was evolved more promptly than in the experiments in which smaller amounts of the sulphuric acid were employed. In Experiments 11 and 12, the greater part of the acid was evolved before heat was applied. These facts seem to be attributable not merely to the increased evolution of heat that takes place when the larger amounts of sulphuric acid are used, but also to the tendency toward the more prompt formation of hydronitric acid in concentrated than in dilute solutions of sulphuric acid, already observed by the authors in connection with their work upon the oxidation of hydrazine sulphate by means of potassium chlorate. In Experiments 6 and 7, the procedure was varied, as follows: The concentrated sulphuric acid was first mixed with the hydrazine sulphate solution in the distilling flask. Through a long-stemmed separatory funnel was then added, drop by drop, 235 cc. of an aqueous solution of potassium persulphate, containing 17.55 grams of the salt per liter. This procedure was shown, however, to be unfavorable to the production of the largest yields of hydronitric acid. In all of the experiments, a slow current of air was drawn through the apparatus to facilitate the quantitative removal of the acid, and after the completion of this operation, the amount of ammonia formed during the reaction was determined by the usual method. The percentage yield of the two substances has been calculated on the basis of the equation



In the last column of Table I it will be observed that the amount of ammonia formed in Experiments 1 and 2 was considerably in excess of the amount required on the basis of the above equation. For the sake of comparison, however, all results have been calculated on the same basis, the abnormal results being designated by placing them in parenthesis.

From the results obtained in the above experiments it is apparent that in general the yield of hydronitric acid varies directly, and the yield of ammonia inversely, with the concentration of the sulphuric acid in the solution, and that the yields of these substances approach equality with each other as the concentration of the sulphuric acid is increased.

Reaction between Hydrazine Sulphate and Potassium Persulphate in Alkaline Solution.—By means of a series of fourteen preliminary qualitative experiments, it was first shown that considerable quantities of ammonia, and small but determinable quantities of hydronitric acid

are usually formed by the action of potassium persulphate upon hydrazine sulphate in the presence of potassium hydroxide. The following solutions were used in these preliminary experiments: hydrazine sulphate, 20 grams per liter; potassium persulphate, 27 grams per liter; potassium hydroxide, 40 grams per 100 cc. In the majority of the experiments, 50 cc. of the hydrazine solution were treated with 100 cc. of the oxidizing solution in the presence of from 1 to 25 cc. of the solution of potassium hydroxide. When the amount of potassium persulphate was increased to 155 cc., no indication of hydronitric acid was obtained. This was also the case when 10 cc. of hydrazine sulphate were treated with 20 cc. of potassium persulphate in the presence of 8 cc. of the potassium hydroxide solution. By proving in the case of a typical experiment that no potassium persulphate remained in the residual alkaline solution, the possible supposition that the hydronitric acid might have been formed by the action of residual potassium persulphate after the solution had been acidified, was rendered untenable.

The amount of hydronitric acid formed was determined in a series of four experiments. In each case, 25 cc. of the potassium hydroxide solution were added drop by drop to a mixture of 100 cc. of the potassium persulphate and 50 cc. of the hydrazine sulphate solution. The reaction was hastened by shaking, and after the evolution of nitrogen was complete, the ammonia formed was distilled into standard acid. To the solution remaining in the distilling flask was then added an excess of sulphuric acid, and the hydronitric acid was distilled into the usual absorbing solution. The amount of hydronitric acid ranged from 0.60 to 1.05 per cent. Some difficulty was experienced in determining the ammonia formed, because of the volatility of hydrazine in alkaline solution. The average yield of ammonia was in the neighborhood of 20 per cent.

On the Use of Hydrazine Sulphate in the Determination of Persulphates.
—Pannain¹ has recently described a method for the determination of persulphates, which is based upon the action of hydrazine sulphate on the persulphates in the presence of potassium hydroxide. The substance to be analyzed, together with the hydrazine sulphate, is placed in the outer compartment of a gas evolution bottle, in the inner compartment of which is placed a solution of potassium hydroxide. The nitrogen evolved after mixing the two solutions, is measured in a Lunge nitrometer. It was taken for granted by Pannain that the hydrazine was completely oxidized, with quantitative evolution of free nitrogen, an assumption seemingly justified by the excellent results obtained by him in a series of twenty-one experiments with ammonium persul-

¹ *Gazz. chim. ital.*, 34, I, 500-4 (1904).

phate, and in a second series of eleven experiments with potassium persulphate. The average error amounted to but + 0.09 per cent. in the first, and to + 0.17 per cent. in the second series.

Rimini¹ has recommended the following procedure, which is to be regarded as a modification of the Pannain method: To a neutral solution of the persulphate is added first a solution of hydrazine sulphate, neutralized with potassium hydroxide, and then a measured quantity of a standard potassium hydroxide solution. After the solution has been shaken, and has been permitted to stand for five minutes, the excess of alkali is determined by titration. The reaction was considered by Rimini to proceed in accordance with the equation



With a solution of potassium persulphate containing 1.76 per cent. of the salt Rimini obtained results varying between 1.657 and 1.562 per cent., corresponding to an error from -5.85 to -11.25 per cent. With an ammonium persulphate solution containing 1.13 per cent. of the salt he twice obtained the result 0.92 per cent., corresponding to an error of about -18.6 per cent. These low results were explained by Rimini himself on the ground that the persulphates analyzed were not absolutely pure.

In the authors' experiments on the reaction between hydrazine sulphate and potassium persulphate in alkaline solution, the conditions were chosen with a view to duplicating, so far as practicable, the conditions prevailing in the work of Pannain and of Rimini, respectively. In these experiments, as has been stated above, it was found that small but determinable amounts of hydronitric acid, and considerable quantities of ammonia were usually formed. The formation of either of these substances during the determination of a persulphate by means of hydrazine sulphate will obviously give rise to error both when the nitrometric method and when the acidimetric method are employed. Any discussion of this error would be foreign to the purpose of the present article, and will consequently be reserved for a later communication, in which the entire subject of the determination of hydrazine and of the use of weighed amounts of hydrazine in the determination of oxidizing agents will be considered from the view-point of analytical chemistry. One precaution that should be borne in mind during the selection of a particular method for either of these determinations is to ascertain whether it is possible, under easily reproducible conditions, to effect the quantitative oxidation of the hydrazine to nitrogen and water. If under the conditions most favorable to this purpose, appreciable quantities of hydronitric acid

¹ *Atti accad. Lincei* [5], 15, II, 320-25; *Chem. Zentralbl.*, 1906, II, 1663.

and ammonia be formed, then the method is as a rule to be regarded with suspicion.

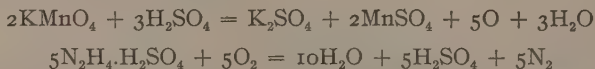
Reaction between Hydrazine Sulphate and Potassium Permanganate in the Presence of Sulphuric Acid.—In 1893, Petersen¹ expressed the reaction between hydrazine sulphate and potassium permanganate in the presence of sulphuric acid by means of the equation



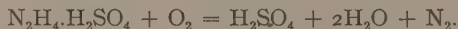
This equation was verified experimentally by determinations of the amount of oxygen consumed, and of the amounts of ammonia and nitrogen formed. The reaction was suggested as the basis of a method for the determination of hydrazine in its salts.

In 1902, Herz² recommended the use of hydrazine sulphate in the determination of potassium permanganate. His procedure consisted in weighing the oxides of manganese precipitated by addition of a soluble carbonate to the solution obtained by treatment of a weighed amount of the permanganate in aqueous solution, with hydrazine sulphate.

In 1904, Roberto and Roncali³ stated that when potassium permanganate is gently heated with hydrazine sulphate, the reaction takes place in accordance with the equations



and that the reaction between hydrazine sulphate and oxidizing agents in general may be expressed by means of the equation



In 1906, Medri⁴ criticized the work of Roberto and Roncali, and further established the equation given by Petersen. He showed, moreover, that the percentage of free sulphuric acid may be varied over a considerable range without influencing the results, but that in the absence of the acid, the oxidation of the hydrazine is more nearly complete.

From the behavior of numerous other oxidizing agents toward hydrazine sulphate under similar conditions, it seems reasonable to suppose that potassium permanganate in acid solution should oxidize hydrazine with the formation of at least small quantities of hydronitric acid. It has already been shown in this laboratory, however, that potassium permanganate is capable of oxidizing hydronitric acid⁵ itself to nitrogen

¹ *Loc. cit.*

² *Ber.*, 35, 949 (1902).

³ *Loc. cit.*

⁴ *Gazz. chim. ital.*, 36, I, 373-8; *Chem. Zentralbl.*, 1906, II, 459.

⁵ Dennis and Browne, *J. Am. Chem. Soc.*, 26, 577 (1904).

and water. Consequently, it was necessary to choose the conditions with a view to permitting the escape of any hydronitric acid that might be formed during the experiment without subjecting the acid to the action of an excess of permanganate.

TABLE II.

No. of experiment.	$\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ (10 grams per liter). cc.	Concentrated H_2SO_4 . cc.	KMnO ₄ (Grams per liter indicated in parenthesis). cc.		Results.
1	100	25	50	(6)	HN ₃ formed
2	100	50	50	(6)	HN ₃ formed
3	100	50	100	(3)	HN ₃ formed
4	100	100	50	(6)	Very little HN ₃ formed
5	100	25	225	(1.5)	HN ₃ formed
6	100	50	225	(1.5)	HN ₃ formed
7	100	0	450	(1.5)	Very little HN ₃ formed
8	50	25	150	(1.2)	HN ₃ formed
9	50	50	150	(1.2)	HN ₃ formed
10	100	5	ca. 150	(2.491)	No HN ₃
11	100	7	ca. 150	(2.491)	No HN ₃
12	100	5	ca. 150	(2.491)	HN ₃ formed
13	100	7	ca. 150	(2.491)	HN ₃ formed

In Table II is recorded a series of qualitative experiments in which the permanganate was added drop by drop after the acidified hydrazine solution had been heated nearly to the boiling point, except in the case of Experiments 10 and 11, in which the solution was held at a temperature of from 60° to 70°, in accordance with the procedure of Petersen. In every experiment except numbers 10 and 11, a distinctly recognizable amount of hydronitric acid, and a large amount of ammonia were obtained.

In two additional experiments, the procedure was reversed by dropping the hydrazine solution into boiling, acidified permanganate. No indication whatever of the formation of hydronitric acid was obtained.

Table III contains the results of several quantitative experiments, in which the amounts of hydronitric acid and ammonia have been determined. In Experiments 1 and 2, the permanganate solution, diluted with an equal volume of water, was gradually added to the boiling, acidified hydrazine solution. The permanganate was diluted in Experiments 3 and 4 with three times, in 5 and 6 with five times, and in 7 to 10 inclusive with one and one-half times its volume of water. In every case the hydronitric acid vapor was drawn over by suction into the usual absorbing solution. In the last two experiments, the hydrazine solution was held at a temperature of from 60° to 70° during the addition of the permanganate.

TABLE III.

No. of experiment.	N ₂ H ₄ .H ₂ SO ₄ (10 grams per liter). cc.	Con- centrated. H ₂ SO ₄ . cc.	KMnO ₄ (6.308 grams per liter). cc.	AgCl obtained. Grams.	Yield HN ₃ . Per cent.	NH ₃ obtained. Gram.	Molecules of NH ₃ per two molecules of N ₂ H ₄ .
1	100	25	62.5	0.0080	1.45	0.10317	1.576
2	100	50	62.5	0.0070	1.7	0.10325	1.578
3	100	25	66.4	0.0157	2.85	0.10156	1.552
4	100	50	64.0	0.0113	2.05	0.10516	1.607
5	100	25	65.0	0.0128	2.32	0.10283	1.571
6	100	50	65.0	0.0176	3.19	0.10240	1.564
7	100	5	64.0	0.0064	1.16	0.10410	1.590
8	100	7	64.0	0.0048	0.87	0.10494	1.603
9	100	5	62.0	..	0.1	0.10812	1.652
10	100	7	62.0	..	0.1	0.10724	1.639

It will be observed that, in general, the yields of hydronitric acid vary inversely with the yields of ammonia. On the basis of the equation suggested by Petersen, the yield of ammonia should amount to 0.10780 gram per gram of hydrazine sulphate, or to 1.647 molecules of ammonia from two molecules of hydrazine. As the yield of hydronitric acid decreases, the yield of ammonia closely approaches this value, as may be noted in the case of Experiments 9 and 10.

In order to ascertain the relative amounts of hydronitric acid, ammonia, and free nitrogen formed under conditions substantially similar to those prevailing in the work already described, a series of experiments were performed in which the reaction was caused to proceed in an apparatus so constructed as to permit the simultaneous determination of these products. A measured, slight excess of the permanganate solution, diluted with five times its volume of water, was slowly added through a dropping funnel to the boiling, acidified solution of hydrazine sulphate, contained in a distilling flask which communicated with a condenser and with the usual absorption apparatus for hydronitric acid. With the aid of a generator modeled after that of Bradley and Hale,¹ the air in the apparatus was displaced with carbon dioxide, and a current of this gas was used throughout each experiment to carry the hydronitric acid into the absorption apparatus, and the nitrogen to the nitrometer tube located at the end of the chain. From the nitrometer, which was filled with a solution of potassium hydroxide at the beginning, the gas was transferred at the end of each experiment to a Hempel gas burette, and was then passed successively into Hempel pipettes filled with potassium hydroxide and with alkaline pyrogallol. The residual gas was assumed to be nitrogen. One nearly constant source of error, which could not be entirely eliminated without the use of rather elaborate precautions, arose from the solubility of atmospheric oxygen and nitro-

¹ *J. Am. Chem. Soc.*, 30, 1090-6 (1908).

gen in the solutions employed. A correction based upon the work of Pettersson and Sonden¹ was consequently introduced in each case.

In Table IV are given the results obtained in these experiments.

TABLE IV.

No. of experi- ment.	N ₂ H ₄ .H ₂ SO ₄ (10 grams per liter). cc.	Con- cen- trated H ₂ SO ₄ . cc.	KMnO ₄ (6.308 grams per liter). cc.	Nitrogen in form of HN ₃ . Gram.	Nitrogen in form of NH ₃ . Gram.	Nitrogen gas.		Total nitrogen account- ed for. Gram.
						cc. (corr.)	Gram.	
1	100	25	62.5	0.00126	0.0892	97.80	0.1223	0.2128
2	100	25	62.0	0.00154	0.0878	97.81	0.1223	0.2116
3	100	10	61.0	0.00079	0.0858	100.96	0.1263	0.2129
4	100	10	61.0	0.00088	..	99.71	0.1247	..
5	100	25	61.0	0.00088	..	100.69	0.1259	..
6	100	50	61.0	0.00127	0.0884	99.47	0.1244	0.2141
7	100	25	61.0	0.00090	0.0866	100.17	0.1253	0.2128
Average (excluding 4 and 5)				0.00115	0.08756		0.12412	0.21284

From the data shown in the last column, it is to be noted that the total amount of nitrogen determined as ammonia, hydronitric acid and free nitrogen, has the average value of 0.21284 gram, or 98.8 per cent. of the theoretical amount, 0.21532 gram. The average result of these experiments may be expressed in round numbers as follows:



It will be seen that seven of the 562 nitrogen atoms, or about 1.2 per cent., have not been accounted for. This error may possibly be explained on the ground that small quantities of other substances are formed during the reaction. It seems more probable, however, that the deficit is to be attributed simply to unavoidable experimental error. For the purpose of the present investigation, the work has demonstrated satisfactorily that the greater part of the hydrazine is converted into nitrogen and ammonia, as stated by Petersen, but that determinable quantities of hydronitric acid are formed under certain conditions.

Reaction between Hydrazine Sulphate and Potassium Permanganate in Alkaline Solution.—Sabanejeff² has utilized potassium permanganate in alkaline solution for the determination of hydrazine in a number of its inorganic compounds. From the circumstance that of nineteen analyses reported in his work, all but one of the results are slightly lower than the theoretical value, showing an average percentage error of about —1.1 per cent., it has seemed possible that at least small quantities of hydronitric acid might be formed during the interaction of the substances. In Table V are shown the results of a series of experiments performed with a view to investigating this possibility.

¹ Ber., 22, 1443 (1889).

² Z. anorg. Chem., 17, 480 (1898); 20, 21 (1899).

TABLE V.

No. of experiment.	N ₂ H ₄ ·H ₂ SO ₄ (10 grams per liter). cc.	KOH (200 grams per liter). cc.	KMnO ₄ (20 grams per liter). cc.	Results.
1	50	10	5	Small amount HN ₃ formed
2	50	10	5	Small amount HN ₃ formed
3	50	10	5	1.2 per cent. HN ₃ formed
4	50	10	5	1.5 per cent. HN ₃ formed
5	50	10	25	Small amount HN ₃ formed
6	50	10	25	Small amount HN ₃ formed
7	50	10	25	Small amount HN ₃ formed
8	50	10	25	Small amount HN ₃ formed
9	50	10	50	No HN ₃ formed
10	50	10	50	No HN ₃ formed
11	50	10	50	No HN ₃ formed
12	50	10	50	Small amount HN ₃ formed

After the addition of the permanganate to the alkaline hydrazine solution in these experiments, the mixture was heated for about half an hour on the steam bath, before the solution was acidified in order to liberate the hydronitric acid formed. In Experiments 5 and 6, the oxides of manganese were removed by filtration before the solution was acidified. In 9 and 10 the excess of permanganate present undoubtedly oxidized the hydronitric acid when the solution was acidified.¹ In 11 and 12, 25 cc. and 75 cc. respectively of a 2 per cent. solution of oxalic acid were added to the solution before acidification.

A second series of experiments, in which potassium hydroxide and potassium permanganate solutions of various concentrations were employed, and in which the temperature was varied from 0° to 100°, has led to the conclusion that, in general, traces of hydronitric acid are formed by the interaction of hydrazine sulphate and potassium permanganate in alkaline solution, provided that the permanganate is not present in excess.

Reaction between Hydrazine Sulphate and Hydrogen Peroxide in the Presence of Sulphuric Acid.—It has already been demonstrated in this laboratory² that considerable quantities of hydronitric acid may be formed by the action of hydrogen peroxide upon hydrazine sulphate in the presence of free sulphuric acid. In a series of ten experiments the yield of the acid as calculated on the basis of the simple equation



was found to vary between 11.4 and 28.4 per cent. This method has since been used repeatedly in this laboratory for the preparation, on a comparatively large scale, of pure solutions of hydronitric acid. In the first series of experiments no attention was given to the possible for-

¹ Dennis and Browne, *Loc. cit.*

² *J. Am. Chem. Soc.*, 27, 551-5 (1905).

mation of ammonia as one of the reaction products. Subsequent experiments have shown, however, that large percentages of ammonia are formed by the reaction.

Two qualitative experiments were first performed, in which 100 cc. of a one per cent. solution of hydrazine sulphate were treated respectively with 5 and 25 cc. of concentrated sulphuric acid. In each case, 10 cc. of 3 per cent. hydrogen peroxide mixed with 15 cc. of water were added to the slowly boiling solution of hydrazine sulphate. The distillate was divided into 30 cc. fractions, each of which was tested for hydronitric acid. In the first experiment, the greater part of the acid was found in the third fraction; in the second experiment, large quantities of the acid were found in the first three fractions. The residual solutions, when made alkaline with sodium hydroxide, were in each case found to contain large amounts of ammonia.

The results obtained in a series of quantitative experiments are presented in Table VI. The yields of hydronitric acid and ammonia have been calculated on the basis of the equation



In comparing these results with the yields of the acid obtained in the earlier work done in this laboratory, it should be borne in mind that when the earlier yields are recalculated on the basis of the new equation, they range from 15.2 to 37.8 per cent., instead of from 11.4 to 28.4 per cent.

TABLE VI.

No. of experiment.	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ (10 grams per liter). cc.	H_2O_2 (3%) cc.	Concentrated H_2SO_4 . cc.	AgCl obtained. Grams.	Yield HN_3 . Per cent.	NH_3 obtained. Gram.	Yield NH_3 . Per cent.
1	100	15	5.0	0.0405	7.35	0.0411	62.8
2	100	15	25.0	0.1579	28.6	0.0379	57.9
3	100	25	15.0	0.1564	28.3	0.0446	68.1
4	100	25	50.0	0.2018	36.6	0.0392	59.8
5	100	20	2.5	0.0323	5.86	0.0717	(109.6)
6	100	20	25.0	0.1673	30.9	0.0515	78.7
7	100	20	50.0	0.2123	38.5	0.0353	53.9
8	100	20	50.0	0.1893	34.3	0.0420	64.1

In all of the experiments except No. 7, the measured quantity of hydrogen peroxide was diluted with twice its volume of distilled water, and the resulting solution was added drop by drop through a separatory funnel, the stem of which extended beneath the surface of the liquid in the distilling flask. Small additional quantities of water were usually added during the progress of the distillation to insure the quantitative removal of the hydronitric acid. After this operation had been completed, 5 cc. of 3 per cent. peroxide solution were added and the distil-

lation was resumed. In no case, however, was the formation of hydronitric acid noted as the result of this procedure, a fact which indicated that sufficient hydrogen peroxide had been previously used in the experiment to effect the complete oxidation of the hydrazine present. In Experiments 7 and 8, 50 cc. of water were distilled from the solution of hydrazine sulphate before the addition of the peroxide solution. In Experiment 7, the peroxide solution was added all at once, and without previous dilution. By this procedure, which exactly duplicated the conditions found in the earlier series of experiments to be most favorable for the production of hydronitric acid, the largest yield of the acid was obtained. It may be said, in general, that the yield of ammonia showed a tendency to vary inversely with the yield of hydronitric acid.

Reaction between Hydrazine Sulphate and Hydrogen Peroxide in Alkaline Solution.—Six qualitative experiments were performed, in which 100 cc. of a one per cent. hydrazine sulphate solution were treated, in the presence of from 2.5 to 25 cc. of concentrated sodium hydroxide solution, with from 30 to 45 cc. of one per cent. hydrogen peroxide. The alkaline hydrazine solution was, in general, heated to boiling, and the peroxide was added drop by drop. The distillate obtained from the alkaline solution was tested for ammonia, and the distillate from the residual solution, after acidification with sulphuric acid was tested for hydronitric acid. In one experiment, in which the peroxide was added to the hydrazine at room temperature, and the mixture permitted to stand over night before distillation, no indication of the formation of hydronitric acid was obtained, although ammonia was found in considerable amount. In the other five experiments, hydronitric acid was formed in small, and ammonia in moderately large quantities. Similar results were obtained when precautions were taken to insure the complete decomposition of the hydrogen peroxide before the solution was acidified.

Reaction between Hydrazine Sulphate and Potassium Perchlorate.—The behavior of these substances in acid solution is illustrated by the experiments recorded in Tables VII and VIII.

TABLE VII.

No. of experiment.	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ (10 grams per liter). cc.	Concentrated, H_2SO_4 . cc.	KClO_4 . Grams.	Results.
1	100	5.0	0.7	Trace HN, NH_3 formed
2	100	10.0	0.7	Trace HN; NH_3 formed
3	100	25.0	7.0	HN_3 and NH_3 formed
4	100	50.0	7.0	HN_3 and NH formed
5	50	12.5	4.0	HN_3 formed
6	50	50.0	6.0	HN_3 formed
7	50	5.0	7.0	HN_3 and NH_3 formed
8	50	10.0	9.0	HN_3 and NH_3 formed

The procedure adopted in these qualitative experiments was briefly as follows: the solid potassium perchlorate was added to the acidified hydrazine sulphate solution, and the successive 30 cc. fractions of the distillate obtained on heating the mixture to boiling were tested for hydronitric acid. In Experiments 3 and 4, the perchlorate was added from time to time in 1 gram portions. Whenever it was found necessary, small quantities of water were added to the reacting mixture during the course of the distillation. The point at which the appearance of the hydronitric acid in the distillate took place was found to depend chiefly upon the concentration of the sulphuric acid.¹ No tests for ammonia were made in Experiments 5 and 6.

TABLE VIII

No. of experi- ment.	N ₂ H ₄ .H ₂ SO ₄ (10 grams per liter). cc.	Concen- trated H ₂ SO ₄ . cc.	KClO ₄ . Grams.	AgCl obtained. Gram.	Yield HN ₃ . Per cent.	NH ₃ obtained. Gram.	Yield NH ₃ . Per cent.
1	100	5	14	0.1237	22.4	0.0257	39.2
2	100	10	14	0.1140	20.7	0.0288	44.0
3	100	15	14	0.0494	8.96	0.0267	40.8
4	100	20	14	0.0510	9.25	0.0276	42.2

In the foregoing experiments, the distillation was effected rather slowly, and small quantities of water were added from time to time to the mixture. In Experiments 3 and 4, some difficulty was experienced owing to the liberation of chlorine. As was expected, the yields of hydronitric acid were found to decrease when the percentage of sulphuric acid was raised so high that the liberation of chlorine in considerable quantity could not well be avoided. After the ammonia had been distilled over, both the residual solution and the distillate were in each case tested for hydrazine, with negative results. It was thus demonstrated that no hydrazine had escaped the action of the oxidizing agent.

It will be observed that the yields of hydronitric acid and ammonia are of about the same magnitude as the yields obtained by the action of potassium chlorate upon hydrazine sulphate.²

Reaction between Hydrazine Sulphate and Sodium Periodate.—In view of the similarity that has been shown to exist between the action of potassium perchlorate and that of potassium chlorate upon hydrazine sulphate, the following experiments have been performed in order to ascertain whether a like relationship could be shown to exist between the behavior of a periodate and that of a typical iodate toward hydrazine sulphate.

Experiment 1.—50 cc. of a 1 per cent. solution of hydrazine sulphate were added drop by drop to an excess of sodium periodate dissolved in

¹ Compare *J. Am. Chem. Soc.*, 30, 57 (1908)

² *Ibid.*, 30, 57 (1908).

50 cc. of water and 5 cc. of concentrated sulphuric acid. Iodine was instantly liberated. No indication of the formation of hydronitric acid was obtained.

Experiment 2.—The conditions prevailing in the preceding experiment were duplicated, but the liberation of iodine was prevented by the addition of solid silver sulphate. Traces of hydronitric acid and ammonia were formed.

Experiment 3.—The acidified periodate solution was added drop by drop to 50 cc. of the hydrazine solution, which had previously been treated with 10 cc. of concentrated sulphuric acid, and heated to boiling. Iodine was liberated, and no indication of the formation of hydronitric acid was obtained.

Experiment 4.—The preceding experiment was duplicated, except for the addition of about one gram of solid silver sulphate to the acidified hydrazine solution prior to the introduction of the periodate solution. No iodine was liberated. Considerable quantities of hydronitric acid and ammonia were formed.

From these experiments it appears that the behavior of sodium periodate toward hydrazine sulphate in acid solution is similar to that of potassium iodate under corresponding conditions, at least so far as the tendency to form hydronitric acid is concerned.¹

Reaction between Hydrazine Sulphate and Lead Dioxide.—In Experiments 2 to 5 inclusive, Table IX, the solid lead dioxide was added to the hydrazine sulphate solution prior to the addition of the sulphuric acid. The solution was then in each case heated to boiling. In Experiments 6 and 7, the dioxide was suspended in 50 cc. of water, the sulphuric acid was added, and finally the hydrazine solution was introduced drop by drop into the mixture which had been heated to a temperature of 90°. The amounts of hydronitric acid formed in this preliminary series of experiments were found to vary in general with the amounts of sulphuric acid added.

TABLE IX.

No. of experiment.	N ₂ H ₄ .H ₂ SO ₄ (to grams per liter). cc.	Concentrated H ₂ SO ₄ . cc.	PbO ₂ Grams.	Results.
1	100	0	4	Small amount HN ₃ formed
2	100	5	4	Considerable HN ₃ formed
3	100	10	4	HN ₃ and NH ₃ formed
4	100	20	4	HN ₃ and NH ₃ formed
5	100	50	4	HN ₃ and NH ₃ formed
6	100	50	4	HN ₃ and NH ₃ formed
7	100	10	4	HN ₃ and NH ₃ formed

¹ *J. Am. Chem. Soc.*, 30, 59 (1908).

By means of suitable blank experiments, it was demonstrated that the lead dioxide employed in this work contained no ammonia. No tests for ammonia were made in connection with Experiments 1 and 2.

In Experiments 2 to 8, inclusive, Table X, the lead dioxide was first added to the hydrazine solution, and then the sulphuric acid was introduced. In Experiments 9 to 12 inclusive an excess of the dioxide suspended in from 80 to 100 cc. of water was added drop by drop to the acidified hydrazine sulphate solution during the process of distillation. The residual solution was filtered in each case before the ammonia was determined.

TABLE X.

No. of experiment.	N ₂ H ₄ .H ₂ SO ₄ (10 grams per liter), cc.	Concentrated H ₂ SO ₄ , cc.	PbO ₂ Grams.	AgCl obtained, Gram.	Yield HN ₃ , Per cent.	NH ₃ obtained, Gram.	Yield NH ₃ Per cent.
1	100	0	4.5	..	..	0.00151	2.3
2	100	10	4.5	0.0090	1.63	0.00667	10.2
3	100	20	6.0	0.0040	0.73	0.00538	8.22
4	100	30	6.0	0.0054	0.98	0.00538	8.22
5	100	40	6.0	0.0064	1.16	0.00495	7.56
6	100	50	6.0	0.0099	1.79	0.00495	7.56
7	100	50	6.0	0.0080	1.45	...	1.1
8	100	50	4.5	0.0086	1.56	...	...
9	100	5	Excess	0.0159	2.88	0.00861	13.2
10	100	10	Excess	0.0167	3.03	0.00710	10.8
11	100	25	Excess	0.0146	2.65	...	...
12	100	50	Excess	0.0226	4.10	0.00628	9.59

Reaction between Hydrazine Sulphate and Red Lead.—Five qualitative experiments were performed, in each of which an excess of red lead suspended in water was gradually introduced into 100 cc. of a boiling, one per cent. solution of hydrazine sulphate, to which a measured amount of concentrated sulphuric acid had previously been added. The amounts of sulphuric acid employed were respectively as follows: 10, 10, 25, 25 and 50 cc. Hydronitric acid was found in each case in the first three or four 30 cc. fractions of the distillate. Ammonia was found in each experiment except No. 5, in which no test was made for it.

Tanatar¹ has shown that both lead dioxide and red lead, as well as chromic acid, hydrogen peroxide, bromine water, and permanganic acid, will oxidize a molecular mixture of hydrazine sulphate and hydroxylammonium chloride, with formation of hydronitric acid.

Reaction between Hydrazine Sulphate and Manganese Dioxide.—In seven preliminary experiments, the two substances were brought together in various ways in the presence of sulphuric acid, with the result that large quantities of ammonia and appreciable amounts of hydronitric acid were usually formed. The yields were determined in a second series of experiments recorded in Table XI.

¹ Ber., 35, 1810 (1902).

TABLE XI.

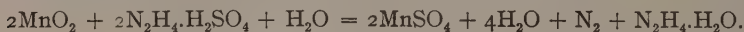
No. of experiment.	N ₂ H ₄ .H ₂ SO ₄ (10 grams per liter). cc.	Concentrated H ₂ SO ₄ . cc.	MnO ₂ . Grams.	AgCl obtained. Gram.	Yield HN ₃ . Per cent.	NH ₃ obtained. Gram.	Molecules of NH ₃ per two molecules N ₂ H ₄ .
1	100	1.0	1.6	0.0076	1.38	0.0433	0.66
2	100	2.5	1.6	0.0081	1.47	0.0521	0.80
3	100	5.0	1.6	0.0128	2.32	0.0588	0.90
4	100	10.0	1.6	0.0068	1.23	0.0551	0.84
5	100	2.5	1.6	0.0072	1.30	0.0545	0.83
6	100	10.0	1.6	0.0060	1.09	0.0717	1.10
7	100	5.0	Excess	0.0095	1.74	0.0899	1.37
8	100	5.0	Excess	..	..	0.0356	0.54
9	100	25.0	Excess	0.0042	0.76	0.1004	1.53
10	100	25.0	Excess	..	..	0.0532	0.81
11	100	2.5	Excess	0.0084	1.52	0.0816	1.25
12	100	2.0	Excess	0.0060	1.09	0.0487	0.74

In Experiments 1 to 4 inclusive, the solid manganese dioxide was suspended in the hydrazine solution, the sulphuric acid was added, and the mixture was gradually heated. Water was added from time to time during the progress of the distillation. In Experiments 5 and 6, the dioxide was suspended in 75 cc. of water, and was treated with the measured amount of sulphuric acid. The mixture was heated to about 90°, and the hydrazine solution was introduced drop by drop. In the remaining experiments, an excess of dioxide, suspended in from 50 to 100 cc. of water, was slowly introduced into the acidified hydrazine sulphate solution. In Experiments 8, 10 and 12, freshly precipitated manganese dioxide was employed. By means of blank experiments, it was demonstrated that neither variety of the dioxide used contained ammonia. Hydronitric acid was formed in Experiments 8 and 10 in sufficient quantity to give the characteristic tests.

Purgotti¹ has recommended the general use of hydrazine sulphate for the gasometric determination of oxidizing agents, relying upon the assumption that the oxidation of hydrazine takes place with quantitative evolution of nitrogen. The action of manganese dioxide upon hydrazine sulphate in acid solution is expressed by this investigator with the aid of the equation:



and the action in neutral solution by the equation:



Summary.

The maximum yields of hydronitric acid and ammonia obtained under specified conditions by the action of certain oxidizing agents upon hydrazine sulphate in aqueous solution, and calculated (when given as percentages) from the equation



are as follows:

(1) With potassium persulphate in acid solution, 40.3 per cent. HN_3 , 1.5 molecules NH_3 from 2 molecules of N_2H_4 ; in alkaline solution, small amounts of HN_3 , and about 20 per cent. of NH_3 .

(2) With potassium permanganate in acid solution, 3.19 per cent. HN_3 , 1.65 molecules NH_3 from 2 molecules N_2H_4 ; in alkaline solution, small amounts of HN_3 .

(3) With hydrogen peroxide in acid solution, 38.5 per cent. HN_3 , 1.10 molecules NH_3 from 2 molecules of N_2H_4 ; in alkaline solution, small amounts of HN_3 , fairly large amounts of NH_3 .

(4) With potassium perchlorate in acid solution, 22.4 per cent. HN_3 , 44.0 per cent. NH_3 .

(5) With sodium periodate in acid solution, considerable quantities of hydronitric acid and ammonia, when silver sulphate was present.

(6) With lead dioxide in acid solution, 4.1 per cent. HN_3 , 13.2 per cent. NH_3 .

(7) With red lead, HN_3 and NH_3 in acid solution.

(8) With manganese dioxide in acid solution, 2.32 per cent. HN_3 , 1.53 molecules NH_3 from 2 molecules N_2H_4 .

CORNELL UNIVERSITY, November, 1908.

ON THE OXIDATION OF HYDRAZINE. III.

Historical.

E. Fischer¹ has shown that by the oxidation of a cold aqueous emulsion of phenylhydrazine with an excess of Fehling's solution, benzene and aniline are formed. Baeyer² has made use of the action of copper sulphate upon the hydrazines in the preparation of hydrocarbons. Gallinek and V. v. Richter³ have called attention to the possible use of copper sulphate in the gasometric determination of the nitrogen in certain hydrazine derivatives. Strache⁴ has suggested the use of hot Fehling's solution in the determination of phenylhydrazine. By measuring the excess of unused phenylhydrazine he has also effected the determination of carbonyl oxygen in aldehydes and in ketones. In a subsequent communication⁵ he calls attention to two possible sources of error in his method, and finally states⁶ that no aniline is formed when boiling hot Fehling's solution is employed, and that the nitrogen is liberated quantitatively under these conditions. A similar method has been applied by Jolles⁷ for the detection and the determination of acetone in urine. Petersen⁸ has described a nitro-metric method for the determination of hydrazine, based upon the action of boiling hot Fehling's solution upon hydrazine salts.

Purgotti⁹ has devised a method for the determination of copper, based upon the reaction expressed by the equation



The solution containing the copper is boiled with the hydrazine sulphate solution in an apparatus modeled after that of Schultze and Tiemann.

Jannasch and Biedermann have¹⁰ shown that copper may be precipitated quantitatively in the presence of sodium hydroxide by addition of a boiling 3 per cent. solution of hydrazine sulphate. This procedure is useful not merely for the determination of copper, but also for the separation of

¹ *Ann.*, **190**, 67-183 (1878).

² See Haller, *Ber.*, **18**, 89-94 (1885). See also Kijner, *J. Russ. Phys. Chem. Soc.*, **31**, 1033-62 (1899); *J. Chem. Soc.*, **78**, I, 333 (1900).

³ *Ber.*, **18**, 3172-78 (1885).

⁴ *Monatsh. Chem.*, **12**, 524-32 (1891). See also de Vries and Hollemann, *Rec. trav. chim.*, **10**, 228-30 (1891); Strache and Iritzer, *Monatsh. Chem.*, **14**, 33-38 (1893); Benedikt and Strache, *Ibid.*, **14**, 270-77 (1893); de Vries, *Ber.*, **27**, 1521-2 (1894); *Ibid.*, **28**, 2611-2 (1895); Kitt, *Chem.-Ztg.*, **22**, 358 (1898); *Chem. Centr.*, **1898**, I, 1310.

⁵ *Monatsh. Chem.*, **13**, 299-315 (1892).

⁶ Strache and Kitt, *Ibid.*, **13**, 316-19 (1892).

⁷ *Z. österr. Apoth. Vereins*, **30**, 198; *Z. anal. Chem.*, **31**, 576 (1892)

⁸ *Z. anorg. Chem.*, **5**, 1-7 (1893).

⁹ *Gazz. chim. ital.*, **26**, II, 559-73 (1896); *Chem. Centr.*, **1897**, I, 487

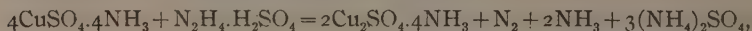
¹⁰ *Ber.*, **33**, 631-36 (1900).

copper from zinc, aluminum, arsenic, and tin. Jannasch and Stephan¹ have studied the separation of platinum from a number of metallic elements, including copper in ammoniacal solution.

Riegler² has recommended the use of an alkaline solution of copper sulphate at room temperature, instead of the hot Fehling's solution, in effecting the gas volumetric determination of acetone in urine.

De Girard and de Saporta,³ referring to the work of Purgotti,⁴ have stated that a double sulphate of copper and hydrazine is formed when a 3.5 per cent. solution of copper sulphate is mixed with a 3 per cent. solution of hydrazine sulphate. They suggest the addition of sodium hydroxide to the solution, in case the reaction is to take place in the cold, and recommend the use of the Trubert calcimeter.

Ebler⁵ has studied the reaction between ammoniacal cupric sulphate and hydrazine sulphate, reaching the conclusion that this reaction proceeds strictly in accordance with the equation



and that quantitative liberation of the nitrogen of the hydrazine consequently takes place. From the results obtained when the copper and when the hydrazine, respectively, are taken in excess, the conclusion is drawn that the method may be employed in the determination either of hydrazine or of copper. In either case the Hempel-Oettel fluorometer is employed.

Rimini⁶ has suggested the use of mercuric chloride in the determination of hydrazine and its derivatives, and has recommended the converse application of the method for the determination of mercury. Ebler⁷ has investigated the reaction between hydrazine sulphate and mercuric chloride under various conditions, with similar objects in view.

The use of hydrazine compounds for the quantitative reduction of

¹ *Ber.*, **37**, 1980-92 (1904). In connection with the further application of hydrazine salts in quantitative analysis, reference should also be made to the other investigations of Jannasch and his co-workers: *Ibid.*, **31**, 2377-94 (1898); **37**, 2210-19, 2219-28, 2441-61 (1904); **38**, 1576-89, 2129-30, 2130-31 (1905). In connection with the application of hydrazine in qualitative analysis see Knoevenagel and Ebler, *Ibid.*, **35**, 3055-67 (1902), and Ebler, *Habilitationsschrift*, Heidelberg, 1905.

² *Z. anal. Chem.*, **40**, 94-7 (1901).

³ *Bull. soc. chim.* [3], **31**, 905-7 (1904). See also Rimini, *Atti accad. Lincei* [5], **14**, I, 386-92 (1905); *Chem. Centr.*, **1905**, I, 1546; Curtius and Schrader, *J. pr. Chem.*, *N. F.*, **50**, 311-346 (1894).

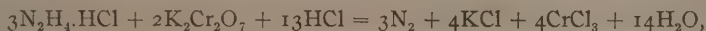
⁴ *Loc. cit.*

⁵ *Z. anorg. Chem.*, **47**, 371-6 (1905).

⁶ *Atti accad. Lincei* [5], **12**, II, 376-81 (1903); *Chem. Centr.*, **1904**, I, 213. See also *Boll. chim. farm.*, **47**, 145-7 (1908); *Chem. Centr.*, **1908**, I, 1797.

⁷ *Z. anorg. Chem.*, **47**, 377-85 (1905). See also Rimini, *Atti accad. Lincei* [5], **15**, II, 320-5 (1906); *Chem. Centr.*, **1906**, II, 1662.

chromates has been suggested by several authorities.¹ The reaction between hydrazine chloride and potassium dichromate in hydrochloric acid solution has been studied by Bach² in connection with his investigation of the heat of formation³ of hydrazine. The reaction is considered to proceed as indicated by the equation



and ammonia is said to be formed in vanishingly small quantities only. Purgotti⁴ has recommended a gas volumetric method for the determination of chromates, depending upon the reaction with hydrazine sulphate in sulphuric acid solution. Tanatar⁵ found that by oxidizing a molecular mixture of hydrazine sulphate and hydroxylammonium chloride in acid solution with chromic acid, considerable quantities of hydronitric acid were obtained. Roberto and Roncali⁶ express the reaction between potassium dichromate and hydrazine sulphate by means of equations substantially identical with that of Purgotti.⁴ Medri⁷ states that hydrazine is completely oxidized by potassium dichromate.

Seubert and Carstens⁸ have studied the velocity of the reaction between hydrazine and chromic acid. Relying upon the observation that the amounts of gas evolved from a given amount of hydrazine chloride in hydrochloric acid solution by the respective action of Fehling's solution and of potassium chromate are the same, they assume that ammonia is not formed as one of the reaction products. From their experimental results these investigators conclude that the reaction is bimolecular, and is to be expressed by the equation



or,



Chattaway⁹ has investigated the behavior of several primary aromatic hydrazines toward a number of oxidizing agents, including free oxygen, metallic oxides, permanganates, and chromates.

¹ Jannasch, "Praktischer Leitfaden der Gewichtsanalyse," 2nd Ed., Veit & Co., Leipzig, 1904, pages 30 and 439; Julius Schmidt, "Die Anwendung der Hydrazine in der Analytischen Chemie," Ferdinand Enke, Stuttgart, 1907, page 19. Herz, *Ber.*, **35**, 949 (1902). See also Curtius and Schrader, *J. pr. Chem., N. F.*, **50**, 311-346 (1894).

² *Z. physik. Chem.*, **9**, 241-63 (1892).

³ See also Berthelot and Matignon, *Ann. chim. phys.* [6], **27**, 289-302 (1892).

⁴ *Loc. cit.*

⁵ *Ber.*, **35**, 1810-11 (1902).

⁶ *L'Industria chimica*, **6**, 178-9 (1904); *Chem. Centr.*, **1904**, II, 616.

⁷ *Gazz. chim. ital.*, **36**, I, 373 (1906); *Chem. Centr.*, **1906**, II, 459.

⁸ *Z. anorg. Chem.*, **56**, 357-364 (1907).

⁹ *J. Chem. Soc.*, **91**, 1323-30 (1907); **93**, 270-80 (1908). See also Zincke, *Ber.*, **18**, 786 (1885); Wurster, *Ber.*, **20**, 2631-3 (1887).

Jannasch¹ has studied the behavior of hydrazine toward selenium and tellurium compounds. Gutbier² has employed a solution of hydrazine hydrate in the determination of tellurium, and in the separation of this element from antimony. Rimini and Malagnini³ have described a selenate of hydrazine, a double selenate of hydrazine and copper, and a double selenate of hydrazine and zinc.

Experimental.

The behavior of hydrazine sulphate in aqueous solution toward a number of oxidizing agents has already been investigated in this laboratory, with especial reference to the formation of hydronitric acid and ammonia.⁴ The substances thus far studied, however, constitute by no means the entire list of oxidizing agents capable of decomposing hydrazine under proper conditions. To make this part of the work more nearly complete it has seemed advisable to put upon record a brief statement of the results obtained in a series of experiments upon the behavior of hydrazine sulphate in aqueous solution toward the following additional substances: cupric sulphate, cupric oxide, Fehling's solution, potassium chromate, mercuric oxide, mercuric chloride, arsenic pentoxide, antimony pentoxide, ozone, chromic sulphate, selenious acid, selenic acid, telluric acid, molybdenum trioxide, ferric oxide, nickel sesquioxide, and cobalt sesquioxide. A number of other substances, including stannic oxide, stannic chloride, sodium bismuthate, tellurous acid, tungsten trioxide, and sodium pyrouanate, gave either indecisive or negative results under the conditions of the experiments performed, and have consequently received no attention in the present article.

The procedure adopted throughout the experiments was similar to that described in the preceding articles, unless otherwise specified. Whenever it seemed at all advisable the materials used were shown by means of suitable tests to be free from ammonia and from nitric acid. The presence of the latter substance might obviously give rise to erroneous conclusions concerning the ability of the oxidizing agent under consideration to form hydronitric acid from hydrazine, as nitric acid itself oxidizes hydrazine with this result. As an illustration of this difficulty it may be said that experiments with sodium metastannate in acid solution resulted in the formation of from 5.7 to 11.5 per cent. of hydronitric acid, while experiments with stannic oxide and stannic chloride gave negative results. It was then found that the sodium metastannate contained appreciable amounts of nitric acid.

The results obtained in the experiments are described under three principal heads: (1) action of cupric compounds upon hydrazine sulphate in alkaline solution; (2) action of potassium chromate upon hydrazine sulphate in acid solution; (3) action of various other oxidizing agents upon hydrazine sulphate in acid or in alkaline solution.

Action of Cupric Compounds upon Hydrazine Sulphate in Alkaline Solution. *Cupric Sulphate.*—A series of experiments was performed in which 50 cc. portions of a solution

¹ *Ber.*, 31, 2386-94 (1898); "Praktischer Leitfaden der Gewichtsanalyse," 2nd Ed., 1904, p. 438; Schmidt, "Die Anwendung der Hydrazine in der Analytischen Chemie," 1907, page 19.

² *Ber.*, 34, 2724-6 (1901); *Z. anorg. Chem.*, 31, 331-9 (1902), foot-note, page 335; 32, 260-71 (1902).

³ *Atti accad. Lincei* [5], 15, II, 561-3 (1906); *Chem. Zentr.*, 1907, I, 86. *Gazz. chim. ital.*, 37, I, 261-6 (1907); *Chem. Zentr.*, 1907, II, 373.

⁴ *J. Am. Chem. Soc.*, 27, 551-5 (1905); 29, 1305-12 (1907); 30, 53-63 (1908); 31, 221-37 (1909).

of hydrazine sulphate (10 gr. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ per liter), to which had been added respectively 0, 5, 7.5, 10, 25, 40, and 50 cc. of a 20 per cent. solution of sodium hydroxide, were treated with an excess of a solution of copper sulphate (22.5 gr. CuSO_4 per liter). This solution was introduced drop by drop into the hydrazine solution, the temperature of which ranged from 20° to 100° in the different experiments. The reaction was in general found to proceed more rapidly as the temperature was raised, and as the concentration of sodium hydroxide was increased. In Experiment 1, in which no sodium hydroxide was used, no reaction was observed to take place. In each of the subsequent experiments the solution was distilled after the addition of the oxidizing agent. In Experiments 2, 3, and 4, the solutions were made strongly alkaline by the use of additional sodium hydroxide prior to distillation. Traces of ammonia were found in the distillates obtained in these experiments, but no ammonia was formed in Experiments 5, 6, and 7. The residual solutions, after acidification with sulphuric acid, were distilled. None of the distillates contained hydronitric acid.

Two additional experiments were performed in which the procedure recommended by Purgotti¹ for the determination of copper in copper salts by the use of hydrazine sulphate in the presence of sodium chloride, was duplicated as nearly as possible. Neither hydronitric acid nor ammonia could be identified as products of the reaction.

Cupric Oxide.—Four experiments were performed in which 50 cc. portions of a one per cent. solution of hydrazine sulphate were warmed gently with an excess of copper oxide in the presence of 0, 2.5, 5, and 25 cc., respectively, of a 20 per cent. solution of sodium hydroxide. In the first experiment no reaction took place, but in the others a slight effervescence began at room temperature, and became more vigorous after the solutions had been heated. In Experiment 2 a copper mirror was deposited on the bottom of the flask. Appreciable amounts of ammonia were formed in the second and third experiments, but no trace of it could be detected in the fourth. No hydronitric acid was formed in any case. A second series of experiments in which freshly precipitated cupric oxide was used, under conditions similar to those just described, gave results substantially identical with those of the first series. Similar results were obtained, moreover, when an aqueous suspension of the copper oxide was introduced gradually into the hydrazine solution instead of being added all at once at the beginning of the experiment.

Fehling's Solution.²—In Table I are summarized the details of a series of experiments upon the behavior of Fehling's solution toward hydrazine sulphate.

TABLE I.

No. of experiment.	$\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ (10 grams per liter). cc.	Fehling's. solution. cc.	Temperature.	Result.
1	50	125	100°	No HN_3 ; trace NH_3 .
2	50	125	100°	No HN_3 ; trace NH_3 .
3	50	125	$15^\circ\text{--}25^\circ$	No HN_3 ; large amount NH_3 .
4	50	125	$50^\circ\text{--}60^\circ$	No HN_3 ; large amount NH_3 .
5	50	125	$60^\circ\text{--}70^\circ$	No HN_3 ; large amount NH_3 .
6	50	125	$85^\circ\text{--}95^\circ$	No HN_3 ; large amount NH_3 .
7	50	125	$85^\circ\text{--}95^\circ$	No HN_3 ; large amount NH_3 .
8	50	125	$85^\circ\text{--}95^\circ$	No HN_3 ; large amount NH_3 .

In Experiments 1 and 2 the hydrazine solution was added drop by drop to the boiling

¹ Loc. cit.

² This solution contained 34.639 grams of copper sulphate, 173 grams of sodium potassium tartrate, and 100 cc. of sodium hydroxide solution (sp. gr. 1.12) per liter,

Fehling's solution, and the mixture was allowed to distil slowly. In Experiments 3 to 8, inclusive, the procedure differed only in that the Fehling's solution was added slowly to the hydrazine solution at the various temperatures indicated. In every case oxidation of the hydrazine took place, but the velocity of the reaction was apparently accelerated as the temperature was raised. No evidence whatever of the formation of hydronitric acid was obtained in any experiment. In Experiments 7 and 8 the Fehling's solution was heated nearly to the boiling point before it was added to the hydrazine. In Experiment 8 the solution of hydrazine sulphate was made strongly alkaline by the addition of 25 cc. of a 20 per cent. potassium hydroxide solution prior to the introduction of the Fehling's solution. The amounts of ammonia formed during the reaction show some tendency to vary inversely with the temperature and with the concentration of the alkali, and are also dependent upon the method employed in bringing the reacting substances together. The results obtained in Experiments 1 and 2 and in other experiments not recorded in the table indicate that only negligible quantities of ammonia and no hydronitric acid whatever are formed when the Fehling's solution is kept at the boiling temperature, and is present in excess at all times during the course of the reaction. From this view-point, then, there can be no possible objection to the use of Fehling's solution, under these conditions, in the determination of hydrazine.

Action of Potassium Chromate upon Hydrazine Sulphate in Acid Solution.—The results obtained in certain typical experiments are shown in Table II.

TABLE II.

No. of experiment.	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ (10 grams per liter). cc.	Conc. H_2SO_4 . cc.	K_2CrO_4 (33 grams per liter). cc.	Result.
1	50	0	45	No HN_3 ; small amount NH_3 .
2	50	10	45	No HN_3 ; large amount NH_3 .
3	50	25	45	Trace HN_3 ; large amount NH_3 .
4	100	2	60	Trace HN_3 ; large amount NH_3 .
5	50	5	excess	No HN_3 ; large amount NH_3 .
6	100	5	75	Small amount HN_3 ; large amount NH_3 .
7	100	25	75	No HN_3 ; large amount NH_3 .
8	100	10	75	37 per cent. NH_3 .
9	100	25	75	66 per cent. NH_3 .

In all of these experiments the chromate solution was added drop by drop to the hydrazine solution. In Experiments 1, 2, 3, 8, and 9, the hydrazine solution was heated to the boiling point; in 4 and 5 it was held at room temperature; in 6 and 7 the temperature was gradually raised, during the addition of the oxidizing agent, from about 20° to 100°. In no case was more than a small amount of hydronitric acid formed, but ammonia was invariably found to be one of the reaction products. The two quantitative experiments, 8 and 9, serve to show the magnitude of the yields of ammonia, and to illustrate the influence of a large excess of sulphuric acid upon the yield. With regard to the effect of temperature it may be said that in general the reaction proceeds more rapidly, and with formation of larger amounts of ammonia, as the temperature is raised. Two additional experiments were performed in which the reacting substances were mixed and were allowed to stand at room temperature for 30 hours. Traces of hydronitric acid and appreciable amounts of ammonia were formed.

By means of a second series of experiments, the details of which are not given in the table, it has been demonstrated that hydrazine dichloride in the presence of hydrochloric acid reacts with chromic acid, yielding considerable amounts of ammonia, and in some instances traces of hydronitric acid. Even at room temperature, under con-

ditions identical with those prevailing in the experiments of Seubert and Carstens,¹ small amounts of ammonia were invariably formed.

In the attempt to throw some light upon the reaction that takes place when hydrazine and hydroxylamine are simultaneously oxidized in acid solution by means of chromic acid,² a number of experiments have been performed, with the following results: (1) Traces, only, of hydronitric acid were formed when hydrazine alone was treated in acid solution with chromic acid; (2) no hydronitric acid was formed when hydrazine and hydroxylamine were heated together in the absence of oxidizing agents, in acid solution; (3) appreciable amounts of hydronitric acid were obtained when hydrazine sulphate in the presence of sulphuric acid was treated at 100° either (a) with the solution obtained by bringing hydroxylamine, in acid solution, into contact with the proper amount of chromic acid to destroy the hydroxylamine without leaving an excess of the oxidizing agent, or (b) with the gaseous oxidation products of the reaction between hydroxylamine and chromic acid in acid solution. Although the amounts of hydronitric acid obtained in the third series of experiments are much smaller than those obtainable by the simultaneous oxidation of hydrazine and hydroxylamine, it seems reasonable to suppose that the formation of the acid may be ascribed, at least in part, to the initial oxidation of the hydroxylamine and subsequent reaction between the hydrazine and the products of the first reaction.

Action of Various Other Oxidizing Agents upon Hydrazine Sulphate. (a) *Mercuric Oxide.*—In the first three experiments 75 cc. of a one per cent. solution of hydrazine sulphate, to which had been added respectively 0 cc., 10 cc., and 25 cc. of concentrated sulphuric acid, were heated in a distilling flask with an excess of red mercuric oxide. In the fourth experiment 10 cc. of a concentrated solution of sodium hydroxide were added instead of the sulphuric acid. In the fifth, sixth, and seventh, 50 cc. of the hydrazine solution, to which 0 cc., 10 cc., and 25 cc. of concentrated sulphuric acid had been added, were heated with an excess of yellow mercuric oxide. In the eighth experiment 20 cc. of the sodium hydroxide solution were added instead of the acid. The hydrazine was oxidized in each case, but no perceptible amount of either hydronitric acid or ammonia was formed during the reaction. When yellow mercuric oxide was added a little at a time, however, to a slightly alkaline solution of hydrazine sulphate held at a temperature of 0°, appreciable amounts of both hydronitric acid and ammonia were formed.

(b) *Mercuric Chloride.*—Three experiments were performed, in which an excess of a saturated solution of the mercuric salt was added drop by drop to 75 cc. of the hydrazine solution containing respectively 0 cc., 10 cc., and 25 cc. of sulphuric acid, and heated to the boiling point. The hydrazine was oxidized, but no hydronitric acid or ammonia could be detected in the products of the reaction.

(c) *Arsenic Pentoxide.*—Fifty cc. portions of the hydrazine sulphate solution were treated respectively with 10 cc. and 25 cc. of sulphuric acid, and were then heated to boiling in the presence of an excess of solid arsenic pentoxide. Distinct indications of the formation of hydronitric acid and ammonia were obtained in each case. The reaction apparently proceeded very slowly.

(d) *Antimony Pentoxide.*—No hydronitric acid was formed when 50 cc. portions of the hydrazine solution in the presence of 10 cc. of sulphuric acid were heated with an excess of sodium pyroantimonate, potassium antimonate, or antimony pentoxide, respectively. In the presence of 10 cc. of a concentrated solution of sodium hydroxide, however, both hydronitric acid and ammonia were formed in each case.

¹ *Loc. cit.*

² Tanatar, *Ber.*, 35, 1810-11 (1902).

(e) *Ozone*.—Several experiments were performed in which ozonized oxygen was passed through acid, neutral, and alkaline solutions of hydrazine sulphate at various temperatures. In every case the hydrazine was gradually oxidized, at a rate that did not appear to undergo any very marked change when the temperature was raised. In one experiment the ozone was passed for over three hours through 100 cc. of a strongly alkaline solution of hydrazine sulphate held at a temperature of from 60° to 90°. Neither hydronitric acid nor ammonia was formed under these conditions, although all of the hydrazine was decomposed. In another experiment, in which an alkaline solution of hydrazine sulphate, heated to the boiling point, was subjected to the action of a current of ozonized oxygen for about 75 minutes, a very appreciable amount of hydronitric acid was obtained. The residual solution was found to contain a considerable quantity of unoxidized hydrazine. In none of the experiments was ammonia positively identified as one of the oxidation products.

(f) *Chromic Sulphate*.—A 50 cc. sample of the hydrazine solution, to which had been added 10 cc. of sulphuric acid, was heated to the boiling point. A solution of chromic sulphate was introduced drop by drop. Shortly before the point in the distillation had been reached at which white fumes began to appear in the flask, hydronitric acid was formed.

(g) *Selenious and Selenic Acids*.—No hydronitric acid was formed in either acid or alkaline solution by the action of selenious acid or of selenium dioxide upon hydrazine sulphate. By the gradual addition of a dilute solution of selenic acid, however, to 50 cc. of the hydrazine solution with 10 cc. or with 15 cc. of sulphuric acid, appreciable amounts of hydronitric acid were obtained.

(h) *Telluric Acid*.—Large quantities of both hydronitric acid and ammonia were formed by the action of an excess of solid telluric acid upon 100 cc. portions of the hydrazine solution, to which had been added from 10 to 25 cc. of sulphuric acid.

(i) *Molybdenum Trioxide*.—In alkaline solution the reaction was found to take place very slowly. Ammonia was found in the products of the reaction, but no hydronitric acid. When 75 cc. portions of the hydrazine solution, acidified respectively with 10 cc. and 25 cc. of sulphuric acid, were subjected to the action of an excess of molybdenum trioxide, appreciable quantities of both hydronitric acid and ammonia were formed. By means of a blank experiment it was shown that the molybdenum trioxide employed in the experiments contained no recognizable trace of ammonia. Two 100 cc. samples of the hydrazine solution were treated with 10 cc. and 25 cc. of sulphuric acid, and were heated to boiling. An excess of the oxidizing agent in the form of an aqueous suspension was added drop by drop. In each case appreciable amounts of hydronitric acid were formed. In the first experiment 26.1 per cent. of ammonia was obtained, and in the second experiment 18.2 per cent.

(j) *Ferric Oxide*.—Three qualitative experiments were first performed in which 75 cc. samples of the hydrazine solution, treated with 5 cc., 10 cc., and 25 cc. of sulphuric acid, were subjected to the action of an excess of hydrated ferric oxide. No trace of hydronitric acid was found in the distillates, but large quantities of ammonia were formed during the reaction. From two 100 cc. samples, similarly oxidized in the presence of 10 cc. and 25 cc. of sulphuric acid, were obtained quantities of ammonia corresponding to a yield of 1.73 and 1.65 molecules of ammonia, respectively, from 2.00 molecules of hydrazine. The ferric oxide and the sulphuric acid used throughout the experiments were found to contain no detectable amount of ammonia.

(k) *Nickel Sesquioxide*.—Three 50 cc. portions of the hydrazine solution, to which had been added 0 cc., 10 cc., and 25 cc. of sulphuric acid, were treated with an excess of nickel sesquioxide, which was suspended in water and added drop by drop. In the third experiment a very faint indication of the formation of hydronitric acid was ob-

tained. In the other two no perceptible trace of the acid was formed. Ammonia was formed in all of the experiments. By means of a blank test it was shown that the oxidizing agent used throughout the work contained no ammonia.

(2) *Cobalt Sesquioxide*.—Three 50 cc. samples of the hydrazine solution, containing 0 cc., 10 cc., and 25 cc. of sulphuric acid were treated with an excess of the oxidizing agent, which was shown by means of a blank experiment to be free from ammonia. In the second and third experiments traces of hydronitric acid were formed. Ammonia was obtained in all of the experiments.

Summary and Discussion of Experimental Results.

In performing the experiments described in the four articles thus far published in the present series the authors have had the following ultimate objects in view:

(1) Investigation of the mechanism of the reaction that takes place between hydrazine and the numerous oxidizing agents under various conditions, and formulation of a suitable theory to account for the observed facts.

(2) Tentative classification of the oxidizing agents on the basis of their behavior toward hydrazine.

(3) Selection of the oxidizing agent best adapted for the preparation of hydronitric acid from hydrazine.

(4) Selection of the oxidizing agent best adapted for the detection of hydrazine.

(5) Study of the reactions that have been used by previous investigators in the determination of hydrazine, or in the determination of certain oxidizing agents.

(6) Expression of the analogy existing between the reactions involved in the oxidation of hydrazine, and those involved in the oxidation of certain organic substitution products of hydrazine.

These topics will now be discussed in the order given.

Mechanism of the Reactions Involved in the Oxidation of Hydrazine.—Methods for the formation of hydronitric acid from hydrazine may be separated into two divisions, according as the other substance used in the reaction does or does not contain nitrogen. The behavior of hydrazine toward such substances as nitrous acid¹ or its salts² and esters,³ nitrogen trichloride,⁴ and nitric acid⁵ has already been studied by previous investigators.

¹ Curtius, *Ber.*, 26, 1263 (1893).

² Angeli, *Atti accad. Lincei* [5], 2, I, 569 (1893); *Chem. Centr.*, 1893, II, 559. Dennstedt and Göblich, *Chem.-Ztg.*, 21, 876 (1897); *Chem. Centr.*, 1897, II, 1093. De Girard and de Saporta, *Bull. soc. chim.* [3], 31, 905-7 (1904). See also Rimini, *Atti accad. Lincei* [5], 14, I, 386-92 (1905); *Chem. Centr.*, 1905, I, 1546. E. Francke, *Ber.*, 38, 4102 (1905).

³ Thiele, *Ber.*, 41, 2681-3, 2806-11 (1908). Stollé, *Ber.*, 41, 2811-13 (1908).

⁴ Tanatar, *Ber.*, 32, 1399 (1899).

⁵ Sabanejeff and Dengin, *Z. anorg. Chem.*, 20, 21 (1899).

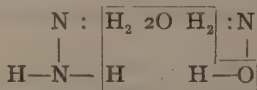
The action of hydrazine upon nitrous acid is assumed by Angeli to be in conformity with the equations



Francke has shown that nitrous oxide and ammonia¹ are formed by the interaction of hydrazine sulphate and sodium nitrite.

Thiele suggests that the formation of nitrous oxide in the experiments of Dennstedt and Göhlich may be due either to the intermediate formation of "dinitrosohydrazine" or to the interaction of hydronitric acid with nitrous acid, the final products in either case being nitrous oxide, nitrogen, and water.

There is still much to be learned concerning the mechanism of the reactions between hydrazine and nitrogen trichloride or nitric acid, and the reactions involved in the simultaneous oxidation² of hydrazine and hydroxylamine. It is impossible at the present time to state with certainty whether or not the nitrogen of these other substances participates in every case in the synthesis of the nitrine group. It is presumable, however, that at least a part of the nitrogen is utilized in this way. If this is true, the reactions involved in the simultaneous oxidation of hydrazine and hydroxylamine, whether explained by a direct condensation as indicated in the following expression



or by the initial formation of nitrous acid, nitric acid, or some other

¹ The formation of ammonia by the action of nitrous acid upon hydrazine has been corroborated by a series of hitherto unpublished experiments performed in this laboratory some months ago by Mr. M. J. Brown. From 115 to 150 cc. of a one per cent. solution of potassium nitrite were introduced drop by drop into 100 cc. portions of a one per cent. solution of hydrazine sulphate containing from 0.5 to 5.0 cc. of concentrated sulphuric acid. The amounts of hydronitric acid formed under these conditions correspond to from 0.18 to 0.28 molecule per molecule of hydrazine used. The amounts of ammonia correspond to from 0.19 to 0.66 molecule per molecule of hydrazine. In the opinion of the authors the reaction between nitrous acid and hydrazine in aqueous solution has not yet been studied under various conditions in sufficient detail to warrant the formulation of a satisfactory hypothesis to account for the observed phenomena. From the facts thus far known it seems reasonable to suppose that while a part of the nitrous acid may act in aqueous solution as ethyl nitrite acts in ethereal solution, condensing with the hydrazine to form hydronitric acid, another part may decompose the hydrazine after the manner of certain oxidizing agents containing no nitrogen, with formation of hydronitric acid and ammonia. It is also conceivable that during this process the nitrous acid might under proper conditions be reduced to hyponitrous acid or nitrous oxide.

² Tanatar, *loc. cit.*

nitrogen compound by oxidation of the hydroxylamine,¹ and subsequent condensation of the hydrazine with these substances, are comparable with the reactions between hydrazine and substances containing nitrogen, rather than with the reactions between hydrazine and nitrogen-free oxidizing agents.

The oxidation of hydrazine by means of substances containing no nitrogen² proceeds in all probability in a different way from that just illustrated. In connection with the work described in the four articles of the present series, the behavior of hydrazine toward more than thirty of these oxidizing agents has been studied with especial reference to the formation of hydronitric acid and ammonia. From this view-point the reaction seems to proceed, with different oxidizing agents in acid solution, in at least three different ways: (a) with formation of fairly large amounts of hydronitric acid and ammonia; (b) with formation of little or no hydronitric acid, but large amounts of ammonia; (c) with formation of little or no hydronitric acid and ammonia. Typical of the oxidizing agents ordinarily reacting with hydrazine in acid solution in the three ways, respectively, are (a) hydrogen peroxide, potassium chlorate, and potassium persulphate; (b) potassium permanganate, manganese dioxide, and ferric oxide; (c) potassium iodate, mercuric oxide, and mercuric chloride.

On the assumption that the first step in the oxidation of a hydrazine molecule is the removal from it of two hydrogen atoms, there are two different ways in which the process of oxidation may be considered to commence. First, by removal of two hydrogen atoms joined to the same nitrogen atom. The residue $H_2:N:N$: might then undergo further loss of hydrogen, with liberation of molecular nitrogen, or else under proper conditions combine, at least transitorily, with another residue of the same sort, forming "tetrazone."³ Second, by removal of two hydrogen atoms joined to different nitrogen atoms. The residue $H.N.N.H$ might then by further oxidation yield free nitrogen, it might take the form of "di-

¹ Bertoni, *Gazz. chim. ital.*, **9**, 571; *J. Chem. Soc. London*, **38**, 298 (1880).

² Ammonium metavanadate in the presence of an excess of sulphuric acid may for the present purpose be included in this class of substances. See *J. Am. Chem. Soc.*, **29**, 1305 (1907).

³ Numerous derivatives of this hypothetical compound, including aliphatic, aromatic, and mixed substitution products, have been prepared, usually by cautious oxidation of unsymmetrical secondary hydrazines with mercuric oxide or ferric chloride. See E. Fischer, *Ann.*, **190**, 67-183 (1878), page 166; **199**, 281-332 (1879), page 319; Renouf, *Ber.*, **13**, 2169-2174 (1880); Michaelis, *Ann.*, **252**, 266-317 (1889); Franchimont and Van Erp, *Rec. trav. chim.*, **14**, 317-26 (1895); Angeli, *Atti accad. Lincei* [5], **9**, II, 180-3 (1900); *Chem. Centr.*, **1900**, II, 857. J. R. Bailey, *J. Am. Chem. Soc.*, **26**, 1006 (1904); **30**, 1412-18 (1908).

imide," $\text{H}\ddot{\text{N}}:\text{N}\ddot{\text{H}}$,¹ or it might unite with another residue of the same sort, yielding "tetrimide." By simultaneous oxidation of "diimide" and hydrazine, with subsequent combination of the residues, it is conceivable that the hypothetical "buzylene"² or "diazohydrazine" might be formed as an intermediate product. The union of $\text{H}_2:\text{N}:\text{N}:$ with $\text{H}\ddot{\text{N}}:\text{N}\ddot{\text{H}}$ would result in the formation of "aminotriimide." The condensation of two "diimide" molecules would yield "diiminohydrazine,"³ $\text{H}\ddot{\text{N}}:\text{N}:\text{N}:\text{N}\ddot{\text{H}}$.

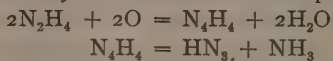
On the assumption that the first step in the process of oxidation is the removal of one hydrogen atom from each of two hydrazine molecules, it is possible that "buzane"⁴ or "hydrotetrazone," $\text{NH}_2\text{NH}\cdot\text{NH}\cdot\text{NH}_2$, might be formed at first, yielding on further oxidation one or more of the intermediate products to which reference has been made in the preceding paragraph.

The behavior of hydrazine toward the three groups of oxidizing agents may be explained as follows:

(a) Oxidizing agents such as hydrogen peroxide, potassium chlorate, and potassium persulphate decompose hydrazine sulphate in acid solution, yielding varying amounts of some such intermediate condensation product

as "buzylene," $\text{HN}:\text{N}\cdot\text{NH}\cdot\text{NH}_2$, or "aminotriimide," $\text{NH}_2\text{N} \begin{array}{c} \text{N}\cdot\text{H} \\ | \\ \text{N}\cdot\text{H} \end{array}$,

which in turn decomposes with formation of hydronitric acid and ammonia. This reaction may be considered to take place in two stages:



The following facts may be cited in support of this hypothesis. E. Fischer⁵ has shown that diazobenzenimide and aniline are obtained by the oxidation of phenylhydrazine under certain conditions. Curtius⁶

¹ The diazo and azo compounds may obviously be regarded as derivatives of this hypothetical compound.

² Derivatives have been prepared by Curtius (*Ber.*, **26**, 1263 (1893)), by Wohl (*Ber.*, **26**, 1587 (1893); see also Wohl and Schiff, *Ber.*, **33**, 2741-58 (1900)), and by Stollé (*J. pr. Chem.* [2], **66**, 332-8 (1902)).

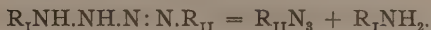
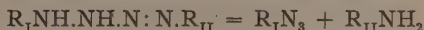
³ Betti, *Gazz. chim. ital.*, **34**, I, 201-12 (1904); *Chem. Centr.*, **1904**, I, 1485.

⁴ Minunni, *Gazz. chim. ital.*, **22**, II, 217-30 (1892); *J. Chem. Soc. London*, **64**, I, 97 (1893); V. Pechmann, *Ber.*, **26**, 1045-7 (1893); V. Pechmann and Runge, *Ibid.*, **27**, 2920 (1894); Ingle and Mann, *J. Chem. Soc. London*, **67**, 606-16 (1895); Minunni and Rap, *Gazz. chim. ital.*, **26**, I, 441-56 (1896); *J. Chem. Soc. London*, **72**, I, 40 (1897); Minunni, *Gazz. chim. ital.*, **27**, II, 215-35, 244-62, 277-92 (1897); **29**, II, 420-34 (1899); *J. Chem. Soc. London*, **74**, I, 190, 191, 192 (1898); **78**, I, 259 (1900); Curtius, *J. pr. Chem.* [2], **62**, 83-126 (1900), page 105.

⁵ *Ber.*, **10**, 1336 (1877).

⁶ *Ibid.*, **29**, 759-83 (1896), page 781.

has obtained similar products by the decomposition of certain buzylenes, and has expressed the reaction by means of the equations

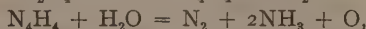


Wohl and Schiff¹ consider that the formation of the azoimides and amines either directly by the action of diazo compounds upon hydrazines, or indirectly by decomposition of the diazohydrazines, is probably due to the intermediate formation of a derivative of the hypothetical com-

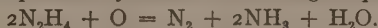
pound $\text{H}_2\text{N.N} \begin{array}{c} \text{N.H} \\ \diagup \quad | \\ \text{N.H} \end{array}$ which breaks up, especially in acid solution, with

formation of the derivatives of hydronitric acid and ammonia.

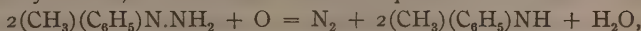
(b) Oxidizing agents of the second class, typified by potassium permanganate, manganese dioxide, and ferric oxide, decompose hydrazine sulphate in acid solution yielding varying amounts of some such intermediate condensation product as "tetrazone," $\text{H}_2\text{N.N:N.NH}_2$, which breaks up under the conditions of the experiment with formation of nitrogen and ammonia. The reaction may perhaps be considered to take place in accordance with the equations



or may be briefly expressed by means of the single equation



In support of this hypothesis may be mentioned the following facts. It has been found by E. Fischer² that during the oxidation of methylphenylhydrazine with mercuric oxide two distinct processes always take place. A part of the hydrazine is decomposed, with formation of nitrogen and methylaniline, in accordance with the equation



while another part yields dimethyldiphenyltetrazone, as follows:



It has been shown, moreover, by the same author, that by heating a dilute solution of tetrethyltetrazone with hydrochloric acid to a temperature of from 70° to 80° , decomposition is effected as indicated by the equation



Renouf³ has studied the decomposition of tetramethyltetrazone in acid solution, and has expressed the reaction by means of an equation corresponding exactly with that given by Fischer for tetrethyltetrazone.

¹ *Loc. cit.*

² *Ann.*, 199, 281-332 (1879), page 323.

³ *Loc. cit.*

(c) Oxidizing agents of the third class, as for example potassium iodate, mercuric oxide, and mercuric chloride, decompose hydrazine sulphate in acid solution at a temperature of 100° apparently without formation of intermediate condensation products. In case such products are formed at first, as might be thought possible in consideration of the behavior of mercuric oxide, for example, toward unsymmetrical secondary hydrazines, it seems certain that they are soon completely oxidized, without formation of hydronitric acid or ammonia.

With certain of the oxidizing agents it seems reasonable to suppose that the reaction may proceed in two ways, or even in all three ways, at once. In general it may be said that the progress of the reaction in any case is very largely influenced by the temperature, by the concentration of the hydrazine, of the sulphuric acid or the alkali, and of the oxidizing agent, by the potential of the oxidizing agent, and by the method adopted in bringing the substances together. Against the possible contention¹ that the differences in the yields of hydronitric acid obtained under different conditions with a given oxidizing agent, or under similar conditions with various oxidizing agents, are to be accounted for wholly or chiefly by the varying oxidizability of hydronitric acid under different conditions, may be cited the following arguments: The amounts of ammonia actually formed by oxidizing agents of the second class are very often considerably larger than the theoretical amount required from those of the first class. Moreover, with a given oxidizing agent of the first class the yields of hydronitric acid usually vary inversely with the yields of ammonia. If the lowering of the yield of hydronitric acid effected by changing the oxidizing agent, or by varying the conditions with a given oxidizing agent, be attributed to the oxidation of the acid, then it would be difficult to account for the concomitant rise in the percentage of ammonia formed, without the assumption that ammonia might be obtained as a product of the oxidation of hydronitric acid. It has already been shown in this laboratory that no ammonia is formed by the oxidation of the acid with potassium permanganate.²

Chattaway³ has explained the behavior of primary aromatic hydrazines toward oxidizing agents on the assumption that one of the hydrogens of the hydrazino group is first attacked, with the result that a hydroxyhydrazine, $R.NH.NH.OH$, is produced. This substance is then supposed to decompose, yielding the corresponding hydrocarbon RH , nitrogen, and water. When a very energetic oxidizing agent is employed, a dihydroxyhydrazine, $R.NH.N(OH)_2$, may be first formed, and this compound may be subsequently broken up so as to form a phenol, nitrogen, and

¹ In this connection see Thiele, *Ber.*, **41**, 2681 (1908).

² Dennis and Browne, *J. Am. Chem. Soc.*, **26**, 577-612 (1904), page 608.

³ *Loc. cit.*

water. This hypothesis is in no way contradictory to that stated in the preceding paragraphs, but it offers no explanation of the nitrogen coupling involved in the formation of hydronitric acid.

Tentative Classification of the Oxidizing Agents on the Basis of Their Behavior toward Hydrazine.—It was at first hoped that it might be possible to establish a simple relationship between the potential of the various oxidizing agents and their ability to produce hydronitric acid from hydrazine. So many different factors have been found to influence the reactions, however, that the project was soon abandoned. In the foregoing paragraphs it has been shown that the oxidizing agents may in general be divided into three classes, the characteristics of which have already been discussed. On the basis of the maximum yields of hydronitric acid obtained in each case, the principal oxidizing agents may be arranged in the following order: Potassium persulphate, 40.3; hydrogen peroxide, 38.5; potassium chlorate, 22.4; potassium perchlorate, 22.4; vanadium pentoxide, 13.6; potassium bromate in the presence of silver sulphate, 11.7; potassium iodate in the presence of silver sulphate, 11.2; potassium bromate, 6.68; lead dioxide, 4.10; potassium permanganate, 3.19; manganese dioxide, 2.32.

One interesting fact that becomes apparent from a study of the numerous oxidizing agents is the similarity that seems to exist between oxidizing agents derived from elements related more or less closely in the periodic arrangement. It has been shown, for example, that the tendency of chlorates, bromates, and iodates, as well as the tendency of free chlorine, bromine, and iodine, to produce hydronitric acid, varies inversely with the atomic weight of the halogen; that while sulphuric acid yields no hydronitric acid, selenic acid yields an appreciable amount, and telluric acid a larger amount of this substance; that the behavior of potassium permanganate is rather similar to that of potassium chromate, while the behavior of ferric oxide is not widely different from that of the nickel and cobalt sesquioxides. Appreciable amounts of hydronitric acid were obtained by the action of the pentoxides of vanadium, arsenic, and antimony. While certain of these apparent analogies may be merely superficial or accidental, it seems probable that the behavior of oxidizing agents toward hydrazine sulphate is at least to some extent dependent upon their position in the periodic arrangement.

Preparation of Hydronitric Acid from Hydrazine.—Hydrogen peroxide has been found to be the most satisfactory of the oxidizing agents studied in the present series, for the preparation of hydronitric acid from hydrazine. Both hydrogen peroxide and hydrazine sulphate are of course readily obtainable in a reasonably pure state, and by means of a single distillation under proper conditions will yield hydronitric acid of a very

fair degree of purity. This method has been repeatedly used for the preparation of the acid in this laboratory under circumstances rendering the convenience of the process and the purity of the product of rather greater importance than the yield of acid obtained.¹ No particular effort has been made, in fact, to increase the yield obtainable by this method, although it is possible that by working in non-aqueous solution, or by using an organic derivative of the oxidizing agent, the yield might be greatly improved. Even if this is found to be true, however, it is very unlikely that from given amounts of hydrazine quantities of hydronitric acid approaching in magnitude those obtained by Thiele and by Stollé² by the action of alkyl nitrites upon hydrazine will ever be obtained. This is chiefly attributable to the inherent difficulty that ammonia is formed by the action of hydrogen peroxide or similar oxidizing agents upon hydrazine, so that yields corresponding to but one molecule of hydronitric acid from two molecules of hydrazine are probably the highest that can be expected. In the method of Thiele, on the other hand, the yield is twice as great as this theoretical maximum, since the nitrogen atoms of both hydrazine and nitrous acid participate in the synthesis of the nitrine ring.

Detection of Hydrazine.—Since the presence of minute amounts of hydronitric acid may be detected by means of the ferric chloride test,³ and since hydrazine may be efficiently converted into hydronitric acid, it is apparent that a possible method for the detection of hydrazine consists in converting this substance into the acid by some convenient method, and then identifying the acid in the usual way. The sensitiveness of the method varies of course with the efficiency of the production of hydronitric acid. The method of Thiele, involving the use of ethyl nitrite, is consequently the one to be recommended when very small amounts of hydrazine are to be detected. In certain cases, however, such substances as nitric acid, hydrogen peroxide or potassium chlorate may be used to advantage in the identification of larger amounts of hydrazine. The presence of hydronitric acid or its hydrolyzable derivatives in the substance to be examined for hydrazine would of course interfere with the test. The presence of sulphocyanic, formic, acetic or meconic acid, or of any other substance giving with ferric chloride a reddish coloration, would necessitate the performance of confirmatory tests,⁴ unless care had been taken at the outset to remove these substances from the sample.

Determination of Hydrazine by Oxidation Methods, and Determination of

¹ See for example Browne and Lundell, *J. Am. Chem. Soc.*, **31**, 435-48 (1909), page 437.

² *Loc. cit.*

³ Dennis and Browne, *Loc. cit.*, page 603.

⁴ See *J. Am. Chem. Soc.*, **27**, 551-5 (1905).

Oxidizing Agents by Reduction with Hydrazine.—On the assumption that hydrazine is completely oxidized to nitrogen and water several different methods for its determination have been based upon the action of oxidizing agents. In some cases ammonia is formed as one of the products of the reaction, and in others both ammonia and hydronitric acid. This is also true in the case of certain reactions in which weighed amounts of hydrazine have been utilized in the determination of oxidizing agents. It is entirely possible, of course, that conditions might be found under which in any of these cases the oxidation might be made complete. Positive proof of the quantitative conversion of the hydrazine to nitrogen and water should be obtained, however, before reliance is placed upon any method which under ordinary conditions is subject to the error just mentioned.

Analogy between Hydrazine and its Substitution Products.—In addition to the analogies to which reference has already been made in this summary, may be mentioned the following: (1) Formation of aniline and ammonia, respectively, by the action of Fehling's solution upon phenylhydrazine¹ and hydrazine; (2) formation of diazobenzenimide and hydronitric acid, respectively, by the oxidation of phenylhydrazine² and hydrazine with hydrogen peroxide; (3) formation of aromatic azoimides and hydronitric acid, respectively, by the oxidation of primary aromatic hydrazines³ and hydrazine with various oxidizing agents.

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¹ E. Fischer, *Ann.*, 190, 67-183 (1878).

² Wurster, *Ber.*, 20, 2631-3 (1887).

³ Chattaway, *Loc. cit.*

